Single-site heterogeneous Cr-based catalyst for the selective trimerisation of ethylene

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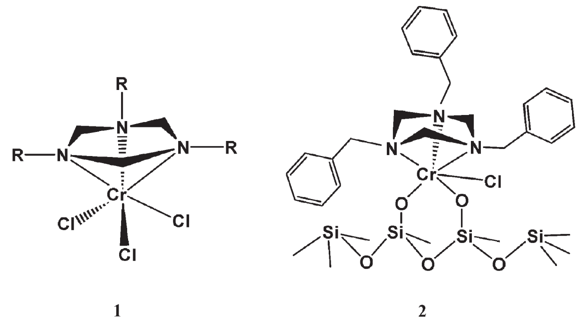
Received (in Cambridge, UK) 26th November 2004, Accepted 26th January 2005
First published as an Advance Article on the web 8th February 2005
DOI: 10.1039/b417938m

TAC–Cr^{3+}/SiO_2 complexes are highly active and selective ethylene trimerisation catalysts and possess single-site catalytic behaviour, an unusual property for heterogeneous catalysts.

α-Olefins, especially 1-hexene, have a high economic value since they are used for, *e.g.*, the production of linear low density polyethylene. Many ethylene trimerisation catalysts are based on homogeneous Cr complexes in which the Cr center is surrounded by either nitrogen,[1] phosphorus,[2] oxygen,[3] sulfur[4] or carbon[5] donor atoms. Although notable progress has been made in homogeneous catalysis, no efficient heterogeneous catalysts have been reported to date. So far, neither trimerisation nor polymerisation single catalysts have been straightforwardly able to selectively produce and consecutively incorporate the trimers into the polymeric structure. As a result, two different catalysts are required as well as the co-feeding with α-olefin–ethylene streams into the industrial reactors. In short, these drawbacks lead to a lower economical efficiency and higher cost prices of polymers. In our opinion, the simultaneous presence of a trimerisation site adjacent to a polymerisation site on a single carrier oxide surface can successfully overcome these problems. Consequently, a heterogeneous one-pot catalytic system for the production of linear low density polyethylenes makes redundant the use of expensive feedstock of 1-hexene as copolymerization agent. Accordingly, the trimer is *in-situ* produced by the trimerisation site, while the polymerisation site sequentially builds it into the polymeric chain. Trimerisation sites can be created by attaching an electron donating ligand onto the regular reduced chromium polymerisation sites.

Here, we report on the first successful heterogeneous Cr-based catalyst for the selective production of 1-hexene. The catalyst consists of a Cr center attached *via* two silanol groups to an amorphous silica carrier and surrounded by three nitrogen atoms of a 1,3,5-tribenzylhexahydro 1,3,5-triazine (TAC) ligand. The donating TAC ligand can form active trimerisation complexes with different metals.[6] The heterogeneous system **2** is more active than its homogeneous counterpart **1**[7] (Scheme 1) and shows a surprising single-site catalytic behaviour for a heterogeneous system. This single-site behaviour also offers a unique possibility to unravel the molecular structure of the active site in great detail; a situation very uncommon in heterogeneous catalysis.[8]

The starting point of our study was a regularly reduced Phillips catalyst (SiO_2: 500 m^2 g^{-1}, 1.5 cm^3 g^{-1}, iso-electric point ~3.2, purity > 99.6%, 1 wt% Cr/SiO_2).[9] It was modified afterwards to assemble a trimerisation site by anchoring a TAC ligand onto highly unsaturated Cr species of the Phillips catalyst. At a Cr : TAC ratio of 1, the catalyst presents predominantly trimerisation centres and has been chosen as a basis to gain insight into the local structure. Special attention has been paid to safe handling the moisture- and air-sensitive catalysts.



Scheme 1 Molecular structure of a homogeneous TAC–$CrCl_3$ complex **1** with R- different alkyl or aryl substituents, together with the proposed molecular structure for the heterogeneous anchored complex **2**.

For reference purposes, we also made complex **1**. Fig. 1 compares the electronic spectra of complex **1** and of the heterogeneous system **2**. The molecular structure of **1** has been described in literature[7] and consists of a regular octahedron CrN_3Cl_3 containing Cr^{III}, which gives rise to two well-defined d–d transitions at 13 900 and 19 700 cm^{-1}. The third allowed d–d transition is overshadowed by an intense charge transfer transition located at 38 000 cm^{-1}. Species **2** has d–d absorption bands at 14 250 and 20 750 cm^{-1}, indicating a strong structural resemblance with **1**. The small band shifts can be explained by the expected replacement of the chloride ligands with silica oxygens. A shoulder

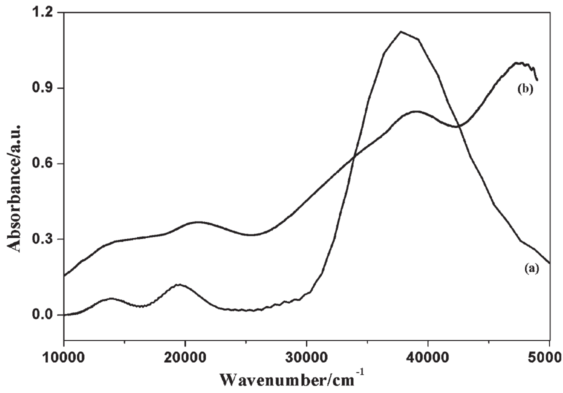


Fig. 1 Electronic spectra of (a) complex **1** and (b) species **2** measured at room temperature.

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at around 28 000 cm^{-1} can also be noted. It was also found that species **2** can be transformed into complex **1** by treating the solid with a saturated hydrochloric acid gas stream. Indeed, the electronic maxima of an HCl-treated species **2** fairly correspond with those of complex **1**.

EXAFS analysis indicated that **2** is linked to two oxygen atoms of silica at a distance of 1.91 Å. Three nitrogen atoms of the TAC ligand were observed at a distance of 2.09 Å, while one chlorine atom originating from a chlorinated solvent completes the coordination sphere at 2.28 Å. Accordingly, the proposed structure of **2** consists of a distorted octahedron of type $CrN_3(O_{silica})_2Cl$ (Scheme 1).[10] The chloride ligand can easily be displaced during reaction, most probably by the co-catalyst developing the structural configuration required for the chromacycloheptane ring formation, which is assumed to be an intermediate mechanistic step in the formation of 1-hexene.[11]

Near edge X-ray absorption spectroscopy at Cr K-edge and Cr $L_{2,3}$-edge proved that the starting chromium site, respectively Cr^{II}, was converted to Cr^{III} upon heterogenisation of the TAC ligand.[10,12]

In order to evaluate the catalytic properties of **1** and **2**, the materials were activated with *N*,*N*-dimethylanilinium tetra-(pentafluorophenyl) borate and triisobutyl-aluminium. Table 1 compares the catalytic activities of both materials under different reaction conditions.[13]

Accordingly, system **2** is highly active towards ethylene trimerisation and produces significant amounts of 1-hexene at 25 and 90 °C. Comparison of the trimerisation turnover numbers (TONs), defined as mole of 1-hexene formed per mole chromium, indicates that species **2** is three times more active than complex **1** under the same reaction conditions. Besides 1-hexene, both systems produce a solid product and traces of heavier oligomers, such as 1-octene, 1-decene, 1-tetradecene and 1-octadecene, but no internal olefins. Therefore, the selectivity in 1-hexene has been estimated towards the free 1-hexene present in the liquid phase.

Table 1 indicates that **2** is very selective towards 1-hexene as selectivity values around 91% were achieved. The enhanced trimerisation activity of **2** at 25 °C compared to those of **1** could be due to the distortion of the Cr coordination induced by the support oxide. Only at 90 °C, the trimerisation selectivity of **2** sustains an appropriate comparison with the trimerisation selectivity of **1**.

Striking differences between **1** and **2** have also been observed with respect to the solid products. The heterogeneous system **2** forms up to three times more solid product compared to **1**, confirming once more its enhanced catalytic activity. In Table 2, these results are presented. However, the noteworthy difference of the two solid products consists in their nature. It is known that **1** forms high-density polyethylene,[14] while species **2** generates only a solid oligomer with an average molecular weight (M_w) of 324 atomic units. DSC measurements showed no well-defined melting temperature for the solid oligomer, but a continuously melting transition from solid to liquid phase in complete agreement with XRD that also shows a total lack of crystallinity. ^{13}C and ^{1}H NMR studies confirmed these results. Both NMR spectra present no relevant resemblance with the NMR spectra of polyethylenes such as LLDPE or HDPE. We consider that 1-hexene and other oligomers, *in-situ* formed, were partially sequentially incorporated into the solid product. In this regard, the trimerisation activity of **2** can be even higher.

Very unexpected is the single-site behaviour of complex **2** indicated by the very low value of the polydispersity index extracted from gel permeation chromatography measurements shown in Fig. 2. Given a M_n (the average molecular number) value of 173 atomic units and a M_w of 324 atomic units, the polydispersity index defined as M_w/M_n is 1.87. This remarkable feature was primarily unforeseen, especially because of the well-known polydisperse nature of our starting material, the reduced Phillips catalyst. Apparently, the coordination of the TAC ligand has drastically narrowed the diversity of the Cr active sites previously existing on the silica surface. Undeniably, it makes **2** noteworthy in heterogeneous catalysis so far as similar catalytic systems have been seldom reported.[8]

One could argue that the catalytic activity of **2** is due to homogeneous Cr species, eventually leached in the liquid solution. Therefore, the heterogeneous nature of species **2** has been

Table 1 Trimerisation activity of the homogeneous complex **1** and of the heterogeneous system **2** at 1 bar

	Temperature/°C	1-Hexene[a]/g	Light oligomers[a]/g	TON (mole 1-C_6/mole Cr)	S_{1C6}[b]
1	25	0.0216	0.0163	2.9	57.0
2	25	0.0158	0.0015	9.6	91.3
2	90	0.0012	0.0011	7.9	52.2

[a] The amount of 1-hexene and of light oligomers was estimated in liquid phase from GC measurements using cyclo-octane as internal standard. [b] Selectivity in 1-hexene was estimated in liquid phase as the percentage amount of 1-hexene reported at the total amount of the obtained products.

Table 2 Polymerisation and oligomerisation activity of the homogeneous complex **1** and heterogeneous system **2** at 1 bar

	Temperature/°C	Solid product/g	Nature of the solid product	PA/OA[a] g mmol Cr^{-1} h^{-1}
1	25	0.94	HDPE	1.74
2	25	1.10	Oligomer	4.40
2	90	1.29	Oligomer	4.64

[a] PA-polymerisation activity of the homogeneous complex **1**; OA-oligomerisation activity of the heterogeneous system **2**.

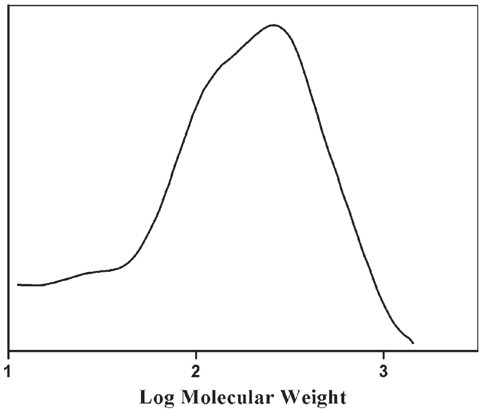

Fig. 2 Gel permeation chromatographic plot of the solid oligomer obtained by **2** at 1 bar, 25 °C and a Cr:TAC ratio of 1.

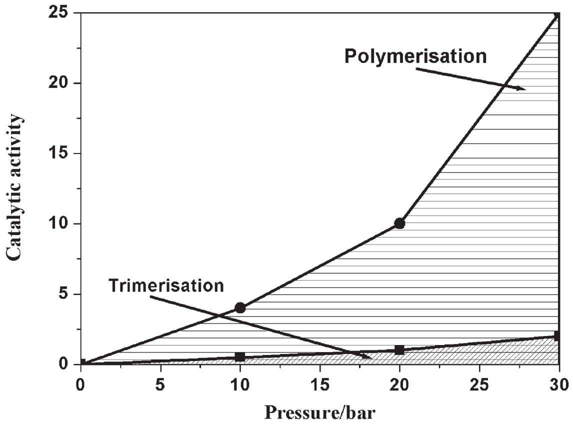

Fig. 3 Trimerisation and polymerization activity of the heterogeneous system **2** as a function of the reaction pressure.

investigated in more detail. For this purpose, we have carried out a catalytic reaction for 0.5 h with species **2**, followed by the transfer of the liquid to a second reactor under inert atmosphere. The reaction was continued for another 0.5 h. The trimerisation activities in both reactors were compared. The second reactor showed no increased trimerisation activity, implying that the solution contained no Cr–TAC complex leached from the first reactor. Chemical analysis with atomic absorption spectroscopy confirmed that no Cr was present into the liquid phase in both reactors.[15]

As can be seen in Table 1, trimerisation activity of species **2** is affected by the higher reaction temperatures leading to a marked decrease of the selectivity in 1-hexene. Therefore, to preserve the high selectivity of **2** in 1-hexene, it is recommended to work at low temperatures. On the other hand, working at higher pressures in an autoclave reactor is not beneficial for the trimerisation system **2** either. Large amounts of solid products are formed and the free 1-hexene which can be retrieved in the liquid phase becomes practically a by-product (Fig. 3). Under these new reaction conditions, the solid product definitely presents a polymeric nature and it presents different characteristics than the heavy oligomer obtained at low pressure. In other words, at high pressures, the trimerisation system **2** is gradually transformed into a polymerisation system which can still produce 1-hexene, although not in high amounts. A similar dual catalytic behaviour was observed also for complex **1** which, under certain reaction conditions, could produce large amounts of polyethylene and can mimic the catalytic behaviour of the Phillips catalyst in the homogeneous phase.[14] No experimental evidence was found that the TAC ligand is leaching at high pressures reconverting species **2** in a regular Phillips polymerisation site. In this view, the heterogeneous system **2** can be considered an active and highly selective trimerisation catalyst only at low pressure. Furthermore, the reaction conditions can be used to turn the catalytic behaviour of **2** towards the desired direction. Finally, we observed that the trimerisation activity of system **2** could be maintained for more than 3.5 h. Futher studies will elaborate on the long term activity and stability of this new catalytic system.

It can be concluded that (1) an ethylene polymerisation catalyst was successfully converted into a truly heterogeneous single-site ethylene trimerisation catalyst upon heterogenisation of a TAC ligand; (2) this catalyst can selectively produce 1-hexene in significant amounts; (3) the solid is three times more active than its homogeneous counterpart; and (4) the heterogeneous system **2** is more active towards trimerisation of ethylene at low pressures and temperatures. Besides the outstanding low dispersity of **2**, the well-defined unique structure of the active site makes the catalyst an excellent system for further structural and *in-situ* mechanistic investigations on ethylene trimerisation reactions. Furthermore, by changing the Cr : TAC ratio we expect to be able to tune the properties of the polymers made.

This work is supported by grants from ATOFINA Research and NWO CW-VICI. The authors thank Ph. Bodart from ATOFINA Research for his valuable comments and suggestions and Prof. D. C. Koningsberger and F.M.F. de Groot for the EXAFS analysis and soft X-ray analysis, respectively.

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