Ethylene Polymerization with Combinations of Early- and Late-Transition Metal Catalysts Immobilized on $MgCl_2$ Supports

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Summary: Immobilization of combinations of early- and late-transition metal catalysts on $MgCl_2$ supports has led to significant increases in catalyst activity when a nickel diimine is incorporated into a Fe-, Cr- or Ti-based catalyst system, and to the formation of intimately mixed, bimodal blends of high- and low-molecular weight polyethylene via coimmobilization of Cr and Fe catalysts.

Keywords: catalyst immobilization; magnesium chloride; metal-organic catalysts/organometallic catalysts; polyethylene (PE); supports

Introduction

Recently, there has been increasing interest in the use of $MgCl_2$-based supports for the immobilization and activation of early- and late-transition metal catalysts for ethylene polymerization.[1–4] Supports of type $MgCl_2/AlR_n(OR')_{3-n}$, obtained either by reaction of an aluminium alkyl with a solid $MgCl_2$/ethanol adduct[5] or a hydrocarbon solution of a $MgCl_2$/2-ethylhexanol adduct,[6] have been found to be effective for the immobilization of a wide range of catalysts and enable the preparation of polymers having controlled particle size and morphology. Our previous studies have included titanium,[7] vanadium,[8] chromium,[9] nickel[10] and iron[11] catalysts.

An interesting feature of immobilized iron catalysts is that their activity in ethylene polymerization increases in the presence of hydrogen. It has been proposed[12] that this results from the reactivation via chain transfer of "dormant" species resulting from 2,1-insertion of vinyl-terminated oligomers into the growing chain. We have similarly observed activation effects of hydrogen in ethylene polymerization with bis(imino)pyridyl iron complexes such as **1** immobilized on $MgCl_2$-based supports, but have now obtained very different results with complex **2**. As a result of the strong influence of ligand steric bulk the latter complex, in which each aryl ring bears only a single *ortho* substituent, gives low molecular weight oligomers rather than polymers.[13] We have observed very high activity in ethylene oligomerization with complex **2** immobilized on a support of type $MgCl_2/AlEt_n(OEt)_{3-n}$ and used in combination with $AlEt_3$ as cocatalyst, but have now found that the addition of hydrogen leads to a large decrease in oligomerization activity, apparent from the data in Table 1. Partial deactivation of oligomer-producing species in iron-based systems will therefore play an important role in hydrogen activation with iron catalysts, reducing the formation of vinyl-terminated oligomers able to insert into the growing polymer chain and form dormant species. Full details of this work have been published elsewhere.[14]

Very high activities can also be achieved in ethylene polymerization with the bis(imino)pyridyl iron complex **1** immobi-

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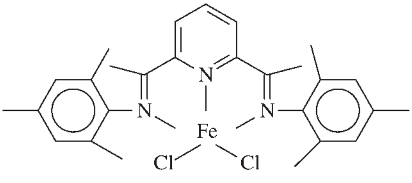

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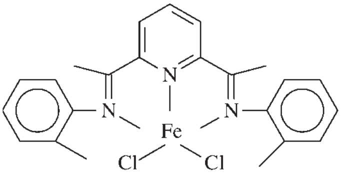

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lized on similar supports.[11] However, the rate of polymerization in ethylene homopolymerization with heterogeneous catalysts can be limited by slow diffusion of the monomer through the crystalline polyethylene formed on the surface and in the pores of the growing particle. This limitation is particularly severe for catalyst supports having low friability.[15] The diffusion limitation can be alleviated by introducing a comonomer, which leads to easier monomer diffusion through the less crystalline copolymer formed, but significant chain branching in polyethylene can also be obtained without the use of comonomer if an α-diimine nickel catalyst is used.[16] The chain branching properties of these Brookhart-type catalysts are also retained after immobilization on a $MgCl_2$ support.[10] It therefore occurred to us that, by incorporating a nickel catalyst into a $MgCl_2$-immobilized iron-based system, the formation of Ni- catalyzed branched polyethylene in the early stage of polymerization may lead to a significant decrease in the monomer diffusion limitation, and thereby to further increases in the productivity of the iron catalyst, with which negligible chain branching is obtained. Results of the coimmobilization of an iron and a nickel catalyst are described below, along with the effects of introducing the nickel component into various $MgCl_2$-supported Ziegler- Natta catalysts.

The aim of incorporating a limited quantity of a nickel complex into an iron- or titanium-based system was not to produce a branched/linear polyethylene blend, but to produce in still higher yield a high-density polyethylene containing a minimal amount of branched polymer. However, the immobilization of two different catalysts on a single support also represents an attractive approach for the preparation, in a single reactor, of bimodal polyethylene. The use of a combination of a chromium and an iron catalyst for the synthesis of bimodal polyethylene, and the effect of the high molecular weight component on shear-induced crystallization, is described in the second part of this contribution.

Experimental Part

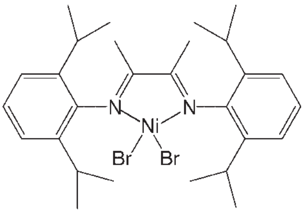
The $MgCl_2/AlEt_n(OEt)_{3-n}$ supports used in this work were prepared by reaction of $AlEt_3$ with an adduct $MgCl_2 \cdot 1.1EtOH$ as described previously.[7] Catalyst immobilization was carried out by contacting the support (100 mg) with 2 mL of a dichloromethane solution containing the desired quantities of the iron or chromium and nickel catalysts at ambient temperature for 16 h. The resulting slurry was, after dilution with light petroleum, used as such in polymerization. In the case of the Ziegler-

Table 1.
Effect of hydrogen on oligomer and polymer formation with complex **2** immobilized on a support of composition $MgCl_2 \cdot 0.17AlEt_{2.25}(OEt)_{0.75}$.

Cocatalyst	H_2 Pressure	Oligomer	Polymer
	bar	kg/mol.bar ethylene.h	kg/mol.bar ethylene.h
$AlEt_3$	0	32950	3800
$AlEt_3$	1	7600	4240
$AliBu_3$	0	9920	3200
$AliBu_3$	1	4960	3840

Natta catalysts of type $MgCl_2$/donor/$TiCl_4$, the catalyst (30–100 mg) was contacted with 0.5 μmol of the Ni complex in 3 mL toluene at room temperature for 16 h.

Polymerization was carried out in a 1 L autoclave by charging the immobilized catalyst, slurried in approx. 100 mL light petroleum, to 400 mL light petroleum containing 1 mmol cocatalyst, at the desired temperature and at an ethylene pressure of 5 bar. Polymerization was continued at constant pressure for 1 h with a stirring rate of 1000 rpm. Investigation of the effects of coimmobilizing a nickel diimine was carried out with $AlEt_3$ as cocatalyst, whereas $Al\mathit{i}Bu_3$ was used as cocatalyst in the preparation of bimodal polyethylene.



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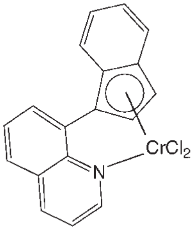

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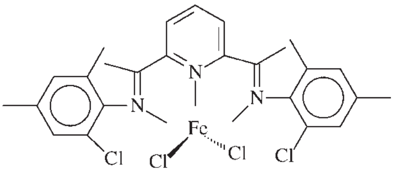

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Wide-angle X-ray diffraction (WAXD) studies of the effect of shear on polyethylene crystallinity development from the melt were performed at beamline ID11 and BM26 at ESRF, Grenoble. A polymer disc 25 mm in diameter and 0.5 mm thick was placed in a Linkam shear cell and heated to 230 °C before cooling to 142 °C at 20 °C/min, then to 137 °C at 10 °C/min. Different shear rates were then applied, after which structural changes were followed by WAXD. The total strain applied was kept constant, varying the applied shear rate from 1 s^{-1} (for 60 s) to 60 s^{-1} (for 1 s).

Synergetic Effects of Nickel Diimine Incorporation

The effects of immobilizing an α-diimine nickel complex together with a bis(imino)-pyridyl iron catalyst were investigated by mixing a support of composition $MgCl_2 \cdot 0.16AlEt_{2.25}(OEt)_{0.75}$ with a dichloromethane solution of **1** and **3**. It was observed that, after contacting overnight at ambient temperature, the colour of the solution was completely transferred to the support, indicating quantitative immobilization. The loading of each catalyst on the support was 5 μmol/g. Polymerizations were carried out at 50, 60 and 70 °C, along with reference experiments in which only the iron complex **1** or the nickel complex **3** was immobilized on the support.

The effect of the presence of the coimmobilized nickel complex on the activity of the iron catalyst is shown in Figure 1. Increases in activity equivalent to around 3000–4000 kg/mol Fe.bar.h, are apparent, much higher than the activities (400–640 kg/mol.bar.h) obtained with only the nickel catalyst, indicating a significant synergetic effect of incorporating a nickel complex into the iron-based catalyst system. No induction period was apparent in these polymerizations and only a very slight decay in activity was observed. Further studies revealed that positive effects on catalyst activity could also be achieved via the incorporation of a nickel complex into immobilized chromium- and titanium-based systems, while fractionation and analysis of the final polymers revealed that these were essentially linear, high-density polyethylenes containing only around 1-3 wt-% branched polymer.[17]

In order to determine whether the productivities of Ziegler-Natta catalysts in ethylene homopolymerization could also be enhanced by incorporation of a nickel complex, various catalysts prepared from different supports and differing in chemical

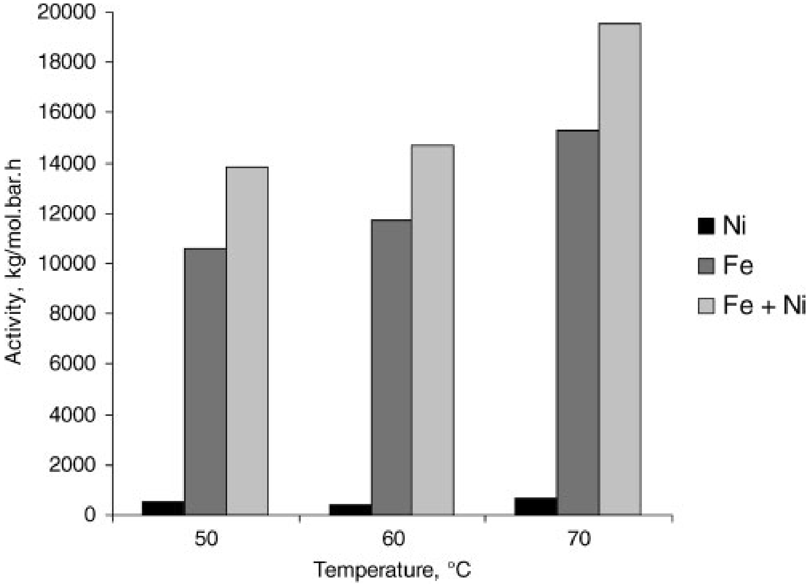

Figure 1.
Ethylene polymerization activities obtained with iron and nickel complexes **1** and **3** immobilized on a support of composition $MgCl_2 \cdot 0.16AlEt_{2.25}(OEt)_{0.75}$. Comparison between single and co-immobilization.

composition were impregnated with complex **3**. Changes in catalyst activity throughout the polymerization were monitored by following variations in the ethylene mass flow required to keep the pressure constant at 5 bar. Typical plots are shown in Figure 2.

It is immediately apparent from Figure 2 that, in contrast to the systems in which a small quantity of an iron or other catalyst is immobilized on a $MgCl_2/AlEt_n(OEt)_{3-n}$ support, the Ziegler-Natta catalysts exhibit acceleration kinetics. In other words, the activity increases throughout the course of polymerization. It is also clear that impregnation with the nickel complex increases Ziegler-Natta catalyst productivity. There are also significant differences between the rate-time profiles. The polymerizations in Figure 2a were carried out using a catalyst prepared by reaction of $TiCl_4$ with a porous, partially dealcoholated support precursor of composition $MgCl_2 \cdot 1.1EtOH$, whereas the catalyst used in Figure 2b was prepared from a support precursor with an $EtOH/MgCl_2$ molar ratio >2. In the absence of the nickel complex, the latter catalyst exhibited low activity, probably due to slow fragmentation of the support. We have noted[17] comparable profiles with other catalysts prepared from similar support precursors; the more pronounced acceleration profile in the presence of complex **3** indicates that particle fragmentation and growth is aided by the formation of Ni-catalyzed branched polyethylene, analogous to the effect of introducing a comonomer.[15]

Bimodal Polyethylene

Bimodal polyethylene comprising a high and a relatively low molecular weight component can be obtained with a single catalyst in a cascade process with two polymerization reactors in series,[18] or via the use of binary catalysts in a single reactor.[19] Immobilization of two different catalysts on a single support represents an attractive approach for the preparation of intimate blends of high and low molecular weight polymers and in the present work we were interested in determining the effect of a high molecular weight fraction on flow-induced crystallization in a polyethylene melt. A combination of the chromium

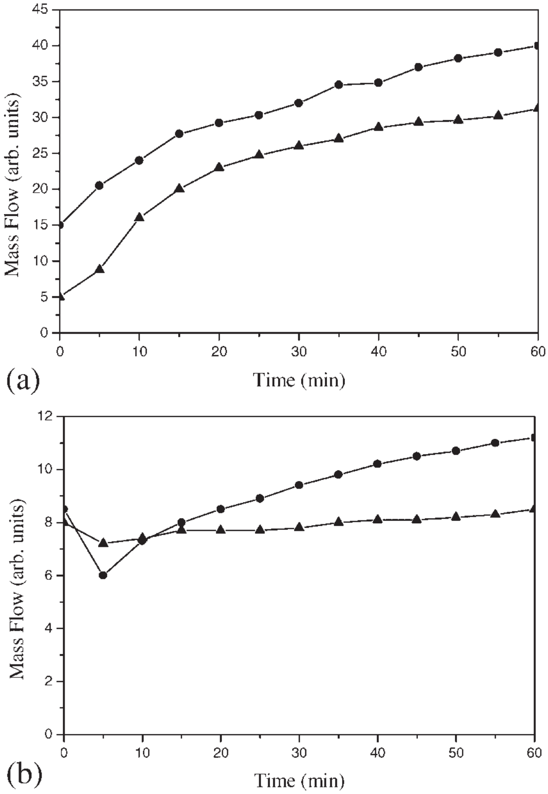

Figure 2.
Rate-time profiles for ethylene polymerizations carried out at 70 °C with Ziegler-Natta catalysts of type MgCl$_2$/diisobutyl phthalate/TiCl$_4$ in the presence (●) and absence (▲) of the Ni complex **3**.

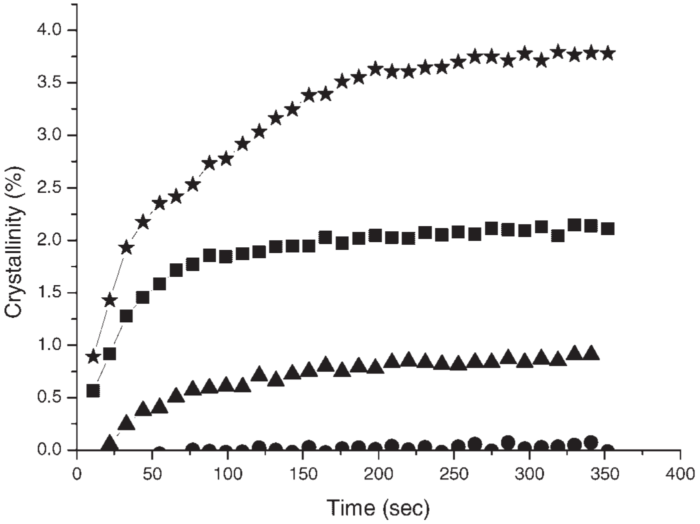

Figure 3.
Evolution of crystallinity as a function of time at 137 °C after applying shear: (●) 1s^{-1}/60 s; (▲) 15 s^{-1}/4 s; (■) 30 s^{-1}/2 s, (★) – 60 s^{-1}/ s.

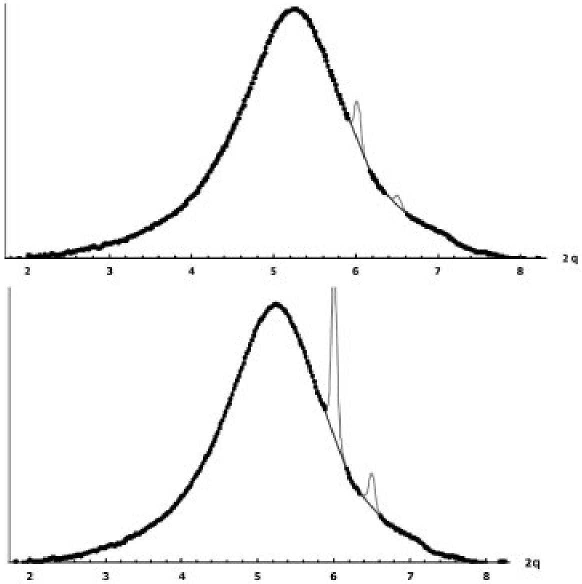

Figure 4.
Integrated WAXD intensities after shear rates of 15 s^{-1} (4 s) and 60 s^{-1} (1 s).

catalyst **4** and the iron catalyst **5** was found to be suitable for this purpose. Previous studies on ethylene polymerization with these catalysts individually immobilized on $MgCl_2/AlEt_n(OEt)_{3-n}$ supports gave molecular weights ($\overline{M}_w$) of around 100,000 and >1,000,000 with catalysts **5** and **4**, respectively.[11,17] We have now seen that the performance and properties of each individual component are retained when the catalysts are coimmobilized on the support, producing bimodal polyethylene. No synergetic effects on polymerization activity were observed in this system; the overall activities corresponded to the sum of the activities of each catalyst component.

A bimodal polyethylene sample containing 10 wt-% of the high molecular weight fraction was selected for WAXD investigation of the effect of shear on flow-induced crystallization in the melt at 137 °C.[20] Figure 3 reveals that the weakest shear did not induce orientation, whereas crystallinity was clearly obtained after increased shear. Taking into account that this experiment was conducted at 137 °C, in other words above the normal melting temperature of polyethylene, the appearance of crystalline diffraction peaks (110 and 200 reflections of the orthorhombic unit cell; Figure 4) can be attributed to orientation of the high molecular weight component under the applied flow conditions. Transmission electron microscopy revealed that after cooling the sheared sample comprised a shish-kebab structure, as has previously been identified in bimodal polyethylenes prepared by solution blending.[21–23] In such bimodal polymers, the long relaxation time of the high molecular weight chains means that the orientation induced by shear is retained, such that crystallization and formation of the shish backbone can occur.

Conclusion

Significant increases in the activities of heterogeneous catalysts for ethylene homopolymerization can be achieved by the incorporation of a diimine nickel catalyst giving branched polyethylene. The increases in activity are ascribed to partial alleviation of the monomer diffusion limitation and to easier particle fragmentation. The synergetic effect is obtained with relatively small quantities of the nickel catalyst, so that the products obtained retain the characteristics of essentially linear, high-density polyethylene.

Shear-induced orientation of the high molecular weight component in a bimodal polyethylene, synthesized via the coimmobilization of a chromium and an iron catalyst on a single $MgCl_2$-based support, results in partial crystallization even at 137 °C. The final crystalline morphology of the polymer has a shish-kebab structure, in which the high molecular weight component forms the shish backbone.

It has also been found that, in contrast to hydrogen activation effects observed with $MgCl_2$-immobilized iron catalysts in ethylene polymerization, the presence of hydrogen in ethylene oligomerization leads to decreased activity. The reduced formation of vinyl-terminated oligomers able to insert at and block polymerization sites therefore plays a significant role in the overall activating effect of hydrogen.

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