$MgCl_2$-Based Supports for the Immobilization and Activation of Nickel Diimine Catalysts for Polymerization of Ethylene

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Recently, there has been increasing interest in late transition metal catalysts for the polymerization of olefins, following the discovery by Brookhart and coworkers of aryl-substituted α-diimine nickel(II) and palladium(II) complexes able to polymerize ethylene to give new types of polyethylene with substantial chain branching.[1,2] The polymer chain microstructure is dependent on the steric bulk of the ortho substituents on the aryl rings and on the polymerization conditions, chain branching increasing with increasing temperature and decreasing ethylene pressure.[3,4]

A prerequisite for the application of these and other single-site catalysts in gas-phase and slurry processes for polyethylene is immobilization on a support.[5] Consequently, several groups have investigated the use of silica supports, most commonly in combination with methylaluminoxane (MAO) as cocatalyst.[6−8] Effective activation of nickel(II) diimine catalysts can also be achieved using diethylaluminum chloride.[9] Recently, alkylaluminum chlorides have been used as cocatalysts for nickel diimine complexes tethered to a silica support pretreated with trimethylaluminum, resulting in productivities of up to 820 kg of PE/g of Ni in 2 h at 60 °C and 150 psig of ethylene, equivalent to an activity of around 2330 kg/mol·bar·h.[10]

We report here on a new and effective method for the immobilization and activation of nickel diimine catalysts, making use of spherical supports of composition $MgCl_2/AlR_n(OEt)_{3-n}$. Such supports are easily prepared by reaction of spherical $MgCl_2$/ethanol adducts with aluminum alkyls.[11] We have recently discovered that Cp_2TiCl_2 and other titanium-based single-site catalysts can be readily immobilized and activated on these supports, without the use of MAO or a borate activator.[12] In the present work, a support of composition $MgCl_2{\cdot}0.24AlEt_{2.3}(OEt)_{0.7}$ was prepared by gradual addition of a 25 wt% solution of triethylaluminum in toluene to a slurry of a spherical adduct $MgCl_2{\cdot}2.1EtOH$ in *n*-heptane at 0 °C, to give a mole ratio $AlEt_3/EtOH = 2$, after which reaction was allowed to continue at room temperature for 2 days with occasional agitation. The solid support was isolated by filtration, washed with *n*-heptane and light petroleum (bp 40−70 °C), and then dried under a flow of argon and subsequently in a vacuum. Catalyst immobilization was carried out by mixing the support (100 mg) with a toluene solution (1 mL) of catalyst (1 μmol) and reacting at 50 °C for 4 h. In each case, complete transfer of the red-brown color from the catalyst solution to the solid support was observed, indicating quantitative catalyst immobilization. The toluene was removed by decantation and the solid (Ni content 0.06 wt %) was reslurried in light petroleum (approximately 50 mL) and charged to a 1 L autoclave containing 450 mL of light petroleum to which 1 mmol of Al-*i*-Bu_3 had been added, at 50 °C and an ethylene pressure of 5 bar, after which polymerization was continued at 5 bar for 1 h.

Chart 1. Nickel(II) Diimine Complexes

(R = *i*-Pr)

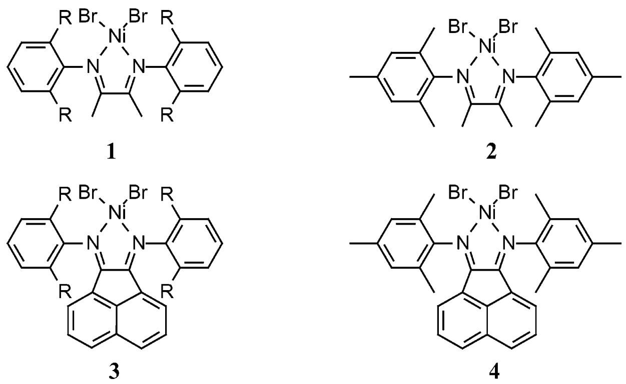

Table 1. Polymerization Results

catal	activity (kg/mol·bar·h)	mp (°C)	M_w (g/mol)	PDI (M_w/M_n)	branches/ 1000 C
1	1190	114.5	1300000	2.3	26
2	4224	121.4	300 000	2.7	11
3	1270	119.8	510 000	2.1	24
4	7158	127.6	290 000	2.9	7
4	11 416[a]				

[a] Polymerization time 30 min.

The catalysts used in this work, prepared according to previously reported procedures,[1,9d] are shown in Chart 1. The polymerization results obtained are given in Table 1. It is evident that very high polymerization activities have been achieved, particularly using complexes **2** and **4**, in which the methyl (as opposed to isopropyl) substituents in the 2,6-positions of the aryl rings give less steric congestion around the metal atom. It is well established that the lifetime of nickel diimine catalysts in ethylene polymerization is limited, particularly at elevated temperatures.[3,4,7,8] Decay in activity during the course of polymerization was similarly apparent in our work, as is evident from the higher activity (expressed per hour) obtained in the 30 min polymerization carried out using complex **4**. With this system the productivity in the second half-hour was around a quarter of that obtained in the first half-hour. Nevertheless, the overall productivities obtained are significantly higher than those previously reported[9d,10] for **4** and analogous complexes, both under homogeneous polymerization conditions and immobilized on silica.

The melting points of the polymers, determined by DSC, indicate different levels of chain branching. Quantitative determination of the types and degrees of branching in these polymers was carried out by ^{13}C NMR. The data in Table 1 indicate the total numbers of branches per thousand carbon atoms in the polymer,

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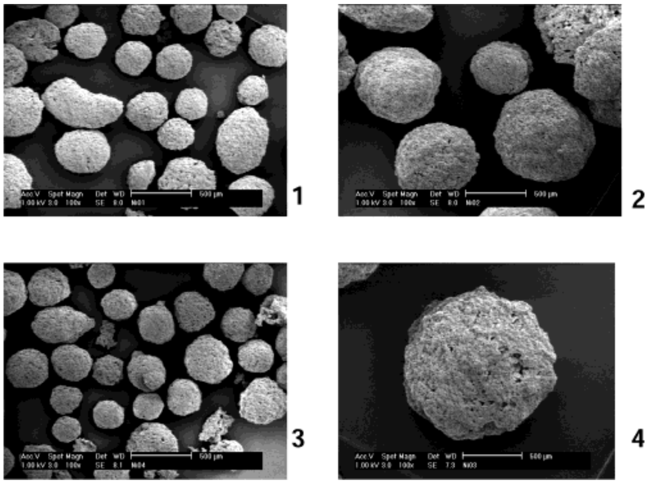

Figure 1. SEM images of polyethylenes prepared using MgCl$_2$-immobilized catalysts **1**−**4**.

Table 2. Polyethylene Branch Distribution

	branch type/1000 C				
catal	methyl	ethyl	propyl	butyl	≥pentyl
1	21.4	1.1	1.0	0.7	2.0
2	9.8	0.8	0.5	0.3	
3	20.6	1.8	0.8	0.2	0.8
4	5.8	0.4	0.3	0.2	

while the branch types and distributions are given in Table 2. It is clear that the polymers prepared using complexes **1** and **3** have relatively high levels of chain branching, induced by the presence of the isopropyl substituents in the ortho positions of the aryl rings[3] and that methyl branches predominate. This is in accordance with previous studies, but the proportion of methyl branches in these polymers, amounting to 82−87% of the total branching, is higher than has been reported for homogeneous systems.[4,7,8,9c,13,14] This may indicate an effect of the support on the chain walking[15] process involving migration of the metal along the alkyl chain, which with nickel(II) diimine catalysts is the cause of chain branching in ethylene polymerization.[3] The data also indicate a small effect of the α-diimine backbone, the acenaphthyl systems **3** and **4** giving less branching than their dimethyl counterparts **1** and **2**.

The polyethylene molecular weight data in Table 1 reveal narrow polydispersities, indicating that the single-site characteristics of the catalysts used are unaffected by immobilization on the support. The polydispersities are narrower than those reported for polymers prepared using silica-supported nickel diimine catalysts.[10] The highest molecular weights were obtained with complexes **1** and **3**, in accordance with previous observations that increased steric bulk in the axial sites leads to a decrease in the rate of chain transfer relative to propagation.[1,3]

The polymers obtained were free-flowing powders and there was no evidence of reactor fouling. Figure 1 shows scanning electron micrographs of the polymer particle morphology, demonstrating retention and replication of the spherical morphology of the original support during catalyst immobilization and polymerization. The SEM images in Figure 1, taken at the same magnification, also illustrate the effect of increasing catalyst productivity on polymer particle size.

In summary, MgCl$_2$/AlR$_n$(OEt)$_{3-n}$ is a simple and effective support for the immobilization and activation of nickel(II) diimine complexes, facilitating their potential use in industrial processes for ethylene polymerization. Very high activities are achieved, along with excellent polymer powder morphology and retention of the single-site characteristics of the catalyst. A patent application has been filed. The use of such supports for a wide range of other polymerization catalysts is under investigation.

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Supporting Information Available: Text giving details of the characterization of polyethylene chain branching using ^{13}C NMR, figures showing ^{13}C NMR spectra of polyethylene prepared by using **1**−**4**, and a chart showing the structures of **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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