

Effect of alkoxysilanes formed in situ on the properties of Ziegler–Natta catalysts for olefin polymerisation

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Abstract

TiCl₄/MgCl₂–alkoxysilane-based catalysts for olefin polymerisation were prepared by supporting TiCl₄ on recrystallised MgCl₂ containing grafted alkoxysilane. The alkoxysilanes were generated in situ during the recrystallisation of MgCl₂ with SiCl₄ from alcoholic solutions. The effect of the nature of the alkoxysilane on the catalytic performance and polymer properties was studied by using different alcohols as solvent. The results of the polymerisation of ethylene and propylene showed that the activities, molecular weights and isotacticities depended strongly on the structure of the alkoxysilane, which possibly acts as an internal electron donor.

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1. Introduction

The use of MgCl₂–alcohol adducts as catalytic supports has attracted a great deal of attention both for the preparation of conventional Ziegler–Natta catalysts [1–13] and for the heterogenisation of metallocenes [14–16]. The main goal of the use of these adducts has been to control the morphology of the resulting polymer and to enhance the activity. The control of morphology is achieved by the replica phenomenon, whereby the polymer formed takes the shape of the catalyst particles [2–5,8,9], whilst increased activity is achieved by generating longer-lived titanium centre [7].

Although Ziegler–Natta catalysts based on TiCl₄/MgCl₂·*n*ROH adduct obtained from recrystallisation methods have the advantage of yielding a good polymer morphology [5,8,9,13], not much progress has been made in terms of activity improvement. It is likely that small amounts of residual alcohol and titanium chloride alkoxides in the support act as catalytic poisons.

In order to overcome the poor activity of Ziegler–Natta catalysts prepared by recrystallisation of MgCl₂ caused by the poisonous effect of residual alcohol and TiCl₄–*n*(OR)_{*n*}, we have previously reported a methodology to prepare a highly active TiCl₄/MgCl₂–alkoxysilane-based catalyst by precipitating the magnesium dichloride from its solution in hexanol with SiCl₄. The silicon tetrachloride reacts with MgCl₂·*n*ROH adduct to form MgCl₂–SiCl₄–*n*(*O*-hexyl)_{*n*}. Then TiCl₄ is supported on the alcohol-free recrystallised MgCl₂–SiCl₄–*n*(*O*-hexyl)_{*n*}. Thus, after a complete dealcoholation, the alkoxysilanes formed remain grafted in the solid catalysts and may act as an electron donor in the catalytic polymerisation [9,11,12].

In this work, we extended our study to investigate the effect of varying the alkoxysilane formed during the synthesis of the solid carrier on the activity of the resultant pre-catalysts and the properties of the polymers obtained. As the alkoxysilane donors are formed from the alcohols used as solvents, variation in the alkoxysilane was achieved by varying the solvent used.

The pre-catalysts were synthesised by supporting TiCl₄ on the alcohol-free modified MgCl₂/alkoxysilane to obtain active catalysts for ethylene and propylene polymerisation.

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The activity of the catalytic systems and the properties of the polymer obtained are discussed as a function of the alcohol used in the preparation of the support.

2. Experimental

2.1. Materials

All manipulations were carried out under an inert atmosphere of N₂ using standard Schlenk techniques. *n*-Heptane, *n*-hexane and isooctane (Aldrich) were distilled under nitrogen over Na/benzophenone and stored over molecular sieves (4 Å). *n*-Hexanol, *t*-butanol, *n*-butanol, 2-propanol, *n*-propanol and ethanol (Aldrich) were distilled under nitrogen before use. Ethylene and propylene (polymerisation grade, Matheson) were passed through columns filled with molecular sieves prior to use.

Titanium tetrachloride, silicon tetrachloride (Aldrich) and triethylaluminum (TEA, Schering) were used without further purification. Anhydrous magnesium dichloride (Aldrich) was dried by heating at 150 °C under vacuum for 48 h.

2.2. Preparation of catalysts

Typically, anhydrous MgCl₂ (1 g, 10.5 mmol) and isooctane (5 ml) were introduced into a three-neck flask equipped with a magnetic stirrer, a reflux condenser and a dropping funnel. With vigorous stirring, the required amount of alcohol (Table 1) was added dropwise. The mixture was then heated to reflux whilst stirring was continued. After complete dissolution of MgCl₂, SiCl₄ in hexane (1:1, v/v) at equimolar ratio SiCl₄/ROH was slowly added to the mixture. A jelly-like precipitate was formed with liberation of HCl fumes. TiCl₄ was then added to the mixture (at an equimolar ratio Ti/Mg) and the reaction mixture was heated to reflux for 2 h with continued vigorous stirring. The reaction mixture was then allowed to cool to room temperature. After reaching room temperature, the precipitate was allowed to settle and the supernatant was removed by filtration. The solid residue was then washed several times with *n*-heptane to remove any excess of TiCl₄ and alkoxy silane.

A pre-catalyst consisting of TiCl₄ supported on MgCl₂ was prepared as a reference catalyst (MT, Table 1). In this case, TiCl₄ was added to the well-stirred suspension of the

MgCl₂ in isooctane, refluxed for 2 h, cooled and washed as described above for the other catalysts.

Finally, catalysts were suspended in *n*-heptane and stored as slurries.

2.3. Polymerisation reactions

The ethylene polymerisations were carried out in a 100 ml Schlenk tube charged with *n*-hexane (50 ml), pre-catalyst (10 μmol) and TEA (5 ml, 1 mmol for a ratio Al/Ti = 100). The reactions were performed under 1 atm of ethylene pressure, with magnetic stirring, at room temperature without temperature control, for 0.5 h.

The propylene polymerisations were carried out in a 1 l stainless steel autoclave (Büchi), which was equipped with a mechanical stirrer and an external jacket connected to a circulating bath for temperature control. The reactor was charged with *n*-hexane (150 ml), pre-catalyst (10 μmol) and TEA (5 ml, 1 mmol for an Al/Ti = 100). The reactions were performed under 9.0 atm of propylene pressure, with mechanical stirring, at 70 °C, for 1 h. During the polymerisations, the temperature was kept within ±0.1 °C.

In both cases, the reactions were terminated by venting the reactor and quenching the polymerisation with a solution of HCl/methanol. The polymer was separated by filtration, washed with methanol and dried in a vacuum oven at 40 °C until it reached constant weight.

2.4. Characterisation

The Ti content of the catalysts was measured using a colorimetric method [17]. After dissolving the pre-catalysts in an acidic media, all of the titanium contained in the catalysts was converted into Ti⁴⁺ by addition of H₂O₂. UV–vis spectra of the resultant solution of peroxo-titanium complexes were recorded on a Perkin-Elmer UV-Lambda 2S spectrometer. The intensity of a peak at 417 nm ($\epsilon = 782.71 \text{ l mol}^{-1} \text{ cm}^{-1}$) was used to quantify the titanium content. Polymer intrinsic viscosities, $[\eta]$, were measured in decaline at 135 ± 0.01 °C, under nitrogen flow, in a PVS1 Lauda viscosimeter. The viscosimetric molecular weight, M_v , was calculated using the Mark-Houwink relation $[\eta] = K(M_v)^\alpha$, $K = 6.7 \times 10^{-4}$ and $\alpha = 0.67$ for polyethylene and $K = 1.1 \times 10^{-4}$ and $\alpha = 0.8$ for polypropylene [18].

Table 1
Composition of MgCl₂–ROH solutions and catalysts

MgCl ₂ :ROH (solutions)	T_{reflux} (°C)	Catalysts	Catalyst component
MgCl ₂		MT	TiCl ₄ /MgCl ₂
MgCl ₂ :4C ₂ H ₅ OH	78–79	MEST	TiCl ₄ /MgCl ₂ –SiCl _{4–n} (EtO) _n
MgCl ₂ :4C ₃ H ₇ OH	96–97	MPST	TiCl ₄ /MgCl ₂ –SiCl _{4–n} (PrO) _n
MgCl ₂ :3C ₄ H ₉ OH	116–118	MBST	TiCl ₄ /MgCl ₂ –SiCl _{4–n} (BuO) _n
MgCl ₂ :3C ₆ H ₁₃ OH	156–157	MHST	TiCl ₄ /MgCl ₂ –SiCl _{4–n} (HexO) _n
MgCl ₂ :16 ⁱ C ₃ H ₇ OH	82–83	MiPST	TiCl ₄ /MgCl ₂ –SiCl _{4–n} (ⁱ PrO) _n
MgCl ₂ :10 ^t C ₄ H ₉ OH	81–82	MtBST	TiCl ₄ /MgCl ₂ –SiCl _{4–n} (^t BuO) _n

The stereoregularity of the polypropylene was estimated by measuring the isotactic index (I.I.). In a typical measurement, 3 g of PP were extracted with boiling *n*-heptane in a Soxhlet apparatus for 8 h. The insoluble fraction was then dried under vacuum and weighed. The I.I. was calculated as the weight percentage of the insoluble polymer in *n*-heptane.

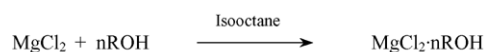
Differential scanning calorimetric (DSC) measurements were recorded on a Rheometric Scientific DSC at a heating rate of 10 °C/min.

3. Results and discussion

The molar ratio of aliphatic alcohol to MgCl₂ required to effect dissolution of the magnesium salt in isoctane varies depending on the alcohol. As can be seen from Table 1, higher ROH/MgCl₂ ratios are required for branched alcohols (entries 6 and 7) than for linear. It is possible that the greater steric bulk of the branched alcohols hampers their diffusion through the MgCl₂ crystal lattice.

It is known that MgCl₂ with a high degree of disorder can be obtained by precipitation of its alcoholic solution [2,3]. It is reasonable to assume that the inclusion of alkoxysilanes in the support will affect the degree of disorder in the support, and that this will very depending on the nature of the alkoxysilane. In turn, the degree of disorder will affect the incorporation of titanium, as titanium is incorporated into defects in the MgCl₂ lattice. This is indeed what is found, the amount of titanium incorporated in all the alkoxysilane-modified catalysts is greater than that in the reference system, and varies from 2.6 wt.% in the ethanol-denned system to 10.8 wt.% in the hexanol-denned system (Table 2).

The synthesis of the TiCl₄/MgCl₂-alkoxysilane catalysts involves three steps (Scheme 1). First, MgCl₂·*n*ROH adducts are formed by dissolving MgCl₂ in the corresponding alcohol [3]. Second, the addition of SiCl₄ results in the precipitation



Scheme 1. Synthesis of the TiCl₄/MgCl₂-alkoxysilane.

of MgCl₂-SiCl₄-*n*(OR)_{*n*} with evolution of HCl. In previous works, we have demonstrated that the addition of SiCl₄ to the hexanol-adduct support leads to a complete dealcoholation by generating alkoxysilane compounds [9–11]. The pre-catalysts prepared in this work using hexanol are reproducible containing similar amount of supported titanium and had the same polymerisation activity when activated. Based on the hexanol results, we presume that upon the addition of SiCl₄ a similar complete dealcoholation occurs regardless of the alcohol used. As a result of this dealcoholation, TiCl₄ impregnation sites are generated in the modified support without, or with minimal, interference from residual alcohol.

In the particular case when hexanol is used as solvent, the following features have been observed: (a) the addition of SiCl₄ to MgCl₂·*n*(C₆H₁₃O) leads to the formation of MgCl₂-SiCl(OC₆H₁₃)₃. This was shown by characterising the recrystallised support by IR spectroscopy [9] and by determining the stoichiometry of the reaction by titration of the HCl liberated [11]. (b) It has also previously been found that after treatment of the support with TiCl₄ and removing any excess of unincorporated TiCl₄ and/or alkoxysilane, the composition of this pre-catalyst determined by X-ray microanalysis (EDX) is: Cl = 64%, Mg = 16%, Si = 9% and Ti = 11% [11]. These results correspond to a stoichiometry of (MgCl₂)_{*a*}(TiCl₄)_{*b*}(Si(OC₆H₁₃)₃)_{*c*}, where *a* = *b* = *c* = 1.

3.1. Ethylene polymerisation

Table 2 shows the results for ethylene polymerisation. The catalytic activity is influenced by the nature of the alkoxysilanes formed during the precipitation of the support, and thus upon the nature of the alcohol used to dissolve the MgCl₂. In general, an increase in activity of the order of 6–11 times, in relation to the reference catalyst, was observed for straight-chain alcohols. The secondary alcohol isopropanol affords an activity value between that of *n*-propanol and *n*-butanol. These results are consistent with the fact that primary and secondary alcohols react readily with SiCl₄ without the formation of side products. The high activity of these catalysts shows that the titanium alkoxide Ti-(OR), which is inactive for polymerisation, is formed in very low quantities, if at all. According to Garoff et al. [19], Cl₃Ti-OR not only increases the catalyst weight, but also blocks the active centres in the activated support material.

Table 2
Results of ethylene polymerisation

Catalysts	Ti (% wt.)	Activity (kgPE/gTi h atm)	T _m (°C)	Δ <i>H</i> _f (J/g)	<i>M</i> _v × 10 ⁻⁶ (g/mol)
MT	1.8	2.03	135	103.6	32.3
MEST	2.6	11.90	136	151.3	8.6
MPST	5.0	16.20	134	152.9	5.6
MBST	3.1	20.88	136	181.8	4.4
MHST	10.8	23.06	134	161.3	5.1
MiPST	4.4	18.40	135	184.7	4.8
MtBST	4.9	2.06	136	135.0	45.0

A much lower activity was obtained when a tertiary alcohol, ^tBuOH, was used. It has been found that tertiary alcohols have a lower reactivity towards the replacement of halogens attached to silicon [20]. Furthermore, when a tertiary alcohol reacts with SiCl₄ an acid acceptor is required to prevent dehydration of the alcohol [21]. Reactive alcohols, such as ^tBuOH, benzyl and 1-phenyl-ethanol, give mainly the alkyl chloride and little or no organosilicon alkoxide when the reaction is carried out in the absence of a base. In this work, instead of using an acid acceptor which would be included in the supported catalysts as a side product, and probably interfere with the polymerisation reaction, an alternative method to remove the HCl liberated from the reaction was used. It consisted of the use of a high-boiling hydrocarbon solvent as media of reaction to reduce the solubility of the hydrogen chloride generated and to avoid the difficult separation of an extra component from the catalyst.

However, it is possible that the dehydration of ^tBuOH occurs to some extent. As a result of the dehydration, an olefin and water are obtained. The water formed can either hydrolyse the organosilicon alkoxide (or chloride) or the MgCl₂ support, generating sites poisonous to TiCl₄. We believe that a combination of these factors, a low level of dealcoholation of the support leading to formation of TiCl₃(OR), hydrolysis of organosilicon alkoxide generated and/or hydrolysis of the MgCl₂, are responsible for the poor activity of MtBST (Table 2).

The viscosimetric molecular weight (M_v), melting temperature (T_m) and heat of fusion (ΔH_f) of the resultant polymers are given in Table 2. The M_v ranged between 440,000 and 860,000 g/mol for the polymers obtained with the more active catalysts (entries 2–6). Interestingly, the less active catalysts, MT and MtBST (entries 1 and 7, respectively), produced polymers with by far the highest polymer molecular weight. These polymers have molecular weights about 6 and 9 times higher, respectively, than those obtained from the other catalysts.

As expected, the polymers with the highest molecular weight showed lower crystallinity (entries 1 and 7, respectively). Higher entanglement of the polymer chains occurs in polymers with high molecular weight; as a result polyethylenes with lower degree of crystallinity are obtained. However, there is a striking difference in the crystallinity of the polymers obtained with the catalysts MT and MtBST. The polymer with the highest molecular weight, obtained with the catalyst MtBST, whilst having the lowest degree of crystallinity of polymers produced by our alkoxy-silane-based catalysts, did not show the lowest degree of crystallinity of all polymers produced. Instead, the polymer obtained with the reference catalyst (MT) showed the lowest crystallinity. It is likely that the polymer formed from the reference catalyst has a different PDI (polydispersity index) to those formed by the alkoxy-silane containing catalysts as this catalyst is chemically different to the others.

In general, the molecular weight varies inversely to activity, as illustrated in Fig. 1. The fact that the activities obtained

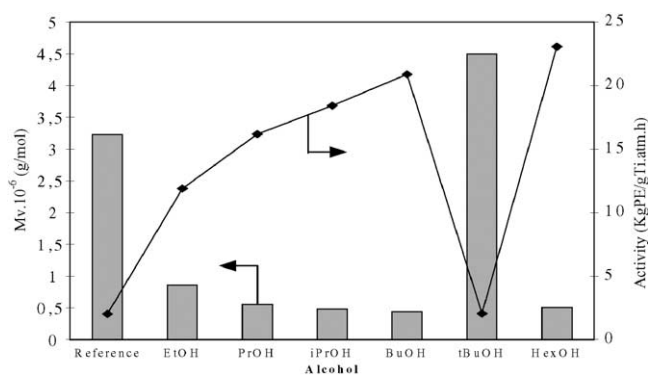


Fig. 1. Activity and molecular weight vs. alcohol used in the synthesis of the support.

with the pre-catalysts containing alkoxy-silane are higher than the one obtained with the reference pre-catalysts is likely to be the result of an internal electron donor modifier leading to an increase in the propagation rate constant.

3.2. Propylene polymerisation

The results of propylene polymerisation using the same catalytic systems are shown in Table 3. As can be seen from the table, the modified catalysts (entries 2–5) were far more active than the reference catalyst. However, catalysts obtained by using ^tBuOH and ⁱPrOH as the dissolving alcohol were inactive toward PP under the experimental conditions used. In general, the same trend of increasing activity with increasing length of the alkyl chain of the dissolving alcohol, that was found for ethylene polymerisation, was observed. However, the molecular weight of the PP seems to have an opposite trend to the one observed for PE. Whilst catalysts prepared by using shorter-chain alcohols produced PE with higher M_v , the M_v of PP was greater for catalysts prepared using dissolving alcohols with longer alkyl chains.

Although, it is clear that alkoxy-silanes generated in situ by reaction of an alcohol adduct of MgCl₂ with SiCl₄ have a beneficial effect on both the activity of the catalysts and the molecular weight of the PP produced, no clear correlations were found between the polymer properties and the nature of the alkoxy-silane donor.

Table 3
Results of propylene polymerisation

Catalysts	Activity ^a	T_m (°C)	ΔH_f (J/g)	%I.I. ^b	$M_v \times 10^{-5}$ (g/mol)	
					PP _{insol+sol}	PP _{insol}
MT	0.3	148	61.4	76	0.56	5.6
MEST	5.3	150	53.1	67	3.47	5.3
MPST	6.4	151	63.1	84	3.87	3.7
MBST	15.8	153	80.3	82	5.45	4.0
MHST	18.9	151	59.4	78	5.18	7.3

^a Activity expressed as kgPP/gTi h atm.

^b Isotacticity index: %I.I. = $(gPP_{insol}/gPP_{sol+insol}) \times 100$, where PP_{insol} = PP insoluble in boiling heptane after extraction and PP_{sol+insol} = PP before extraction.

Efforts to elucidate the characteristics and performance of this new generation of stereospecific catalysts in order to optimise both activity and stereocontrol are currently in progress and will be the subject of further reports.

4. Conclusions

A convenient methodology to prepare heterogeneous Ziegler–Natta TiCl_4 -based catalysts supported on a modified MgCl_2 containing alkoxy silane has been developed. This methodology affords highly active catalysts for olefin polymerisation with the further advantage that there is no interference caused by an excess of the modifier during the impregnation of TiCl_4 . The nature of the alkoxy silane generated in situ during the synthesis of the catalysts has an appreciable effect on the catalyst activity and molecular weight of PE. No clear correlation could be established between the nature of the electron donor and the properties of PP.

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