ACS Catalysis

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Effect of Aluminum Alkyls on a Homogeneous and Silica-Supported Phenoxy-Imine Titanium Catalyst for Ethylene Trimerization

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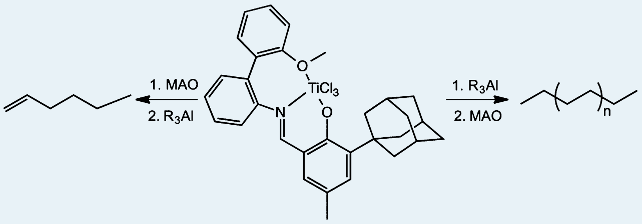


ABSTRACT: A phenoxy-imine titanium catalyst (FI-catalyst) for selective ethylene trimerization was immobilized on methyl aluminoxane (MAO) pretreated silica and its activity and selectivity was compared with that of the corresponding homogeneous catalyst system. The homogeneous and heterogeneous ethylene oligomerization was conducted in the presence of different aluminum alkyls, commonly used as scavengers during olefin polymerization to remove residual oxygen and moisture from the reaction medium. Both the homogeneous and heterogeneous catalysts were strongly affected by the presence of scavenger in the reaction medium. Upon activation with R_3Al/MAO (R= Et, *n*Oct, *i*Bu), the homogeneous catalyst switches selectivity from ethylene trimerization to polymerization. NMR spectroscopic investigations indicate that this change of selectivity can be attributed to ligand exchange between the precatalyst and the aluminum alkyl and reduction of the titanium species. The thereby formed ligand-free and/or reduced titanium alkyls act as polymerization catalysts and are responsible for the increasing polymer formation. Using the heterogeneous catalyst, the scavenger employed during ethylene trimerization was found to be of crucial influence regarding the activity of the catalyst and the occurrence of reactor fouling. Employing aluminum alkyls like *i*Bu_3Al and *n*Oct_3Al resulted in catalyst leaching and homogeneous polymer formation. The latter was prevented using Me_3Al or Et_3Al as scavengers; however, in general the supported catalyst was poisoned by aluminum alkyls, resulting in a low overall activity. It was found to be beneficial for the heterogeneous trimerization system to employ silica-supported scavengers. By physical separation of the catalyst and the scavenger this poisoning effect was effectively prevented, resulting in a highly active heterogeneous catalyst.

KEYWORDS: *selective ethylene oligomerization, supported catalyst, silica, phenoxy-imine titanium catalyst, aluminum alkyls*

INTRODUCTION

The selective oligomerization of ethylene yielding α-olefins like 1-hexene and 1-octene has attracted significant attention due to the demand of these products as comonomers for the production of LLDPE, a copolymer of ethylene and higher α-olefins.[1] A large number of selective oligomerization catalysts have been reported in the literature. Although the field of selective ethylene trimerization and tetramerization is dominated by chromium-based catalysts,[2,3] several examples of selective ethylene trimerization using titanium complexes are reported in the literature. Early examples are $Cp^*TiMe_3/B(C_6F_5)_3$ and $PhMeCCpTiCl_3$/methyl aluminoxane (MAO),[4−6] while more recently Fujita and co-workers at Mitsui reported a highly active and selective ethylene trimerization phenoxy-imine titanium complex (FI-catalyst, **1**).[7,8]

However, even the most selective ethylene oligomerization catalysts generally yield small amounts of polyethylene as a side product. Using homogeneous catalysts these trace amounts of polyethylene tend to precipitate without morphology control on the inner parts of the reactor (reactor fouling). Although these traces of homogeneously formed polymer appear harmless on a laboratory scale, reactor fouling can seriously disturb a continuous industrial process. Preventing reactor fouling is therefore an important issue in ethylene oligomerization.[9−12]

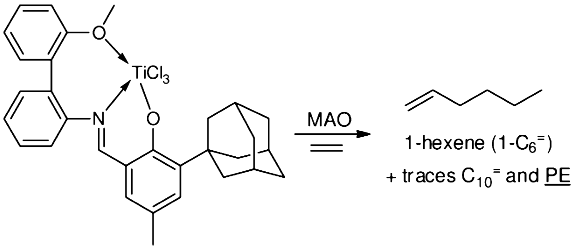
Employing supported rather than homogeneous catalysts during olefin polymerization effectively prevents reactor fouling.[12−21] The same could well be true during ethylene oligomerization. While the immobilization of single-site catalysts for olefin polymerization is well-documented in the literature, immobilization of oligomerization catalysts has hardly been addressed. Some examples are given in the literature involving supported cocatalysts for the activation of chromium-based[10−12] or titanium-based[4−6] ethylene oligomerization catalysts, while the immobilization on silica of a chromium catalyst for ethylene trimerization has been described by Monoi and Sasaki.[22] Furthermore, the tethering of chromium-based catalysts on polymeric supports has been described.[23,24] However, none of the authors comment on the morphology of the polymeric side product, catalyst leaching or reactor fouling during the oligomerization process.

Received: March 1, 2015
Published: July 21, 2015

DOI: 10.1021/acscatal.5b01359
ACS Catal. 2015, 5, 5068−5076

Here we report the immobilization of the Mitsui ethylene trimerization precatalyst **1** (Scheme 1), with the aim to prevent reactor fouling by homogeneous polymer formation while retaining the high trimerization activity and selectivity.

Scheme 1. Titanium-Based Selective Ethylene Trimerization Catalyst Employed in This Study



RESULTS AND DISCUSSION

Preparation and Characterization of the Supported Catalyst. The FI precatalyst **1** was immobilized on silica via a two-step process as illustrated in Scheme 2. First silica-supported MAO was prepared by impregnating the calcined SiO_2 (600 °C) with MAO at elevated temperature (90 °C). Subsequently, the catalyst precursor was contacted with the silica-supported MAO to yield the final silica-supported **1**. The porosity of the support material and the immobilized catalysts were characterized via N_2 physisorption while the metal loading was determined by elemental analysis (Table 1). Whereas the overall surface area (S_p) of the silica did not change significantly upon immobilization of MAO and the catalyst precursor, both the pore diameter (d_p) and pore volume (V_p) reduced by ~50%. The applied immobilization method for MAO resulted in an aluminum content of 12.7 wt % for the supported cocatalyst, which did not change significantly (0.14 wt %) despite thorough washing of the supported MAO and the immobilized **1**. The titanium content of the catalyst was determined to be 0.18 wt %, resulting in a molar Al/Ti-ratio of 121.

Figure 1 shows the infrared spectra (DRIFT) of the support material, supported MAO and the immobilized catalyst. The spectra of the calcined silica mainly features a sharp peak at 3747 cm^{-1} which can be assigned to the OH-vibration of isolated and geminal silanol groups, which are the main surface species after calcination at 600 °C.[25] Furthermore, a broad and weak band around 3680 cm^{-1} can be detected, which can be assigned to intraglobular silanol groups. After treatment of the silica with MAO the peak of the isolated and geminal surface silanol groups has disappeared, indicating their quantitative reaction with the MAO. The broad peak around 3670 cm^{-1} was retained indicating that some intraglobular silanol groups do not react with MAO.[26] Three new peaks at 2954, 2901, and 2844 cm^{-1} appeared after the impregnation of the support material with MAO and can be assigned to the CH vibration of aluminum methyl species bound to the silica surface. Reaction of the silica-supported MAO with **1** does not change the DRIFT spectrum. Peaks that could be assigned to the catalyst are not visible due to the low concentration of the supported catalyst.

Homogeneous Catalyst and Effect of Different Aluminum Alkyls. During initial experiments, homogeneous **1**/MAO was tested as benchmark varying both the reaction temperature and ethylene pressure to identify the optimal reaction conditions to achieve the highest activity and selectivity for ethylene trimerization (Table 2).

Temperature was found to have the largest influence on the selectivity of the catalyst, with the highest trimerization selectivity at low temperature. This can be explained by thermal instability of the ethylene trimerization catalyst, which has also been observed in other titanium-based ethylene trimerization systems.[5,6,23] Ethylene pressure showed a lesser effect on selectivity but a dramatic effect on the activity of the catalyst.

The large excess of MAO applied in homogeneous catalysis is usually sufficient to scavenge residual impurities.[28−30] When supported catalysts, which generally have a much lower MAO/catalyst ratio, are employed it is essential to add an additional scavenger (typically a trialkyl aluminum). However, the latter can significantly influence the reactivity of homogeneous[31−37] and heterogeneous catalysts.[38−43] To elucidate the influence of scavengers on the selectivity or activity of **1**, the homogeneous system was tested in the presence of different aluminum alkyls. Besides commonly applied scavengers such as triethylaluminum (Et_3Al), trioctylaluminum ($nOct_3Al$) and triisobutyl aluminum (iBu_3Al) also trimethylaluminum (Me_3Al) was tested. Although the latter is a key ingredient in MAO, it is usually not applied as scavenger in heterogeneous catalysis due to its known detrimental effect on some olefin polymerization catalysts.[33,36,37,44]

The response of **1** to different concentrations of aluminum alkyls in homogeneous catalysis is summarized in Table 3. Entry 1 of Table 3 illustrates the reference-experiment using an excess of MAO (Al_{MAO}/Ti = 2250) without the addition of aluminum alkyls. Under the given standard conditions the catalyst produced 93.3 wt % of 1-hexene with an overall activity of 10.2 kg·mmol(Ti)$^{-1}$·h^{-1}. As side products, branched decenes (5.1 wt %) and polyethylene (1.6 wt %) were formed. In the presence of 0.1 mmol of Oct_3Al the trimerization selectivity

Scheme 2. Support of MAO and 1 on SiO_2

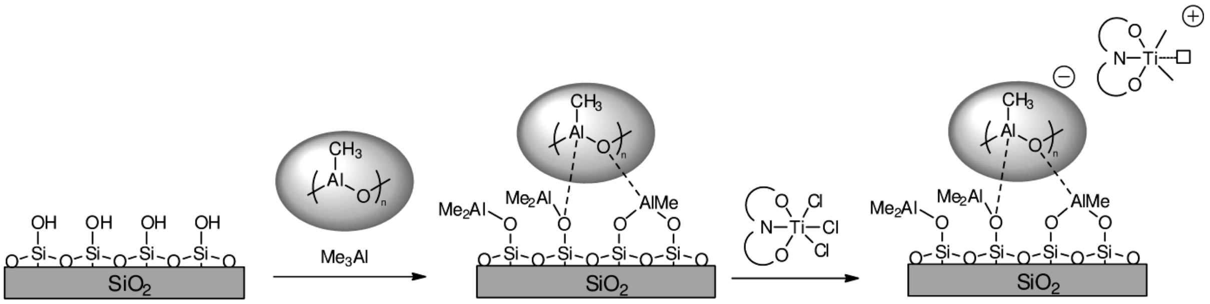


Table 1. Porosity and Elemental Composition of Support Material and Supported Catalyst

	porosity (BJH)[a]			composition[b]				
				Al		Ti		
support/catalyst	S_p (m^2/g)	d_p (nm)	V_p (cm^3/g)	(wt %)	(mmol/g)	(wt %)	(μmol/g)	Al/Ti
SiO_2	299	22.2	1.66					
MAO/SiO_2	306	11.7	0.90	12.66	4.7			
1/MAO/SiO_2	307	10.9	0.84	12.52	4.6	0.18	38	121

[a]Pore surface area (S_p), pore diameter (d_p), and pore volume (V_p) obtained via N_2-physisorption (BJH-theory, values from adsorption). [b]Elemental analysis.

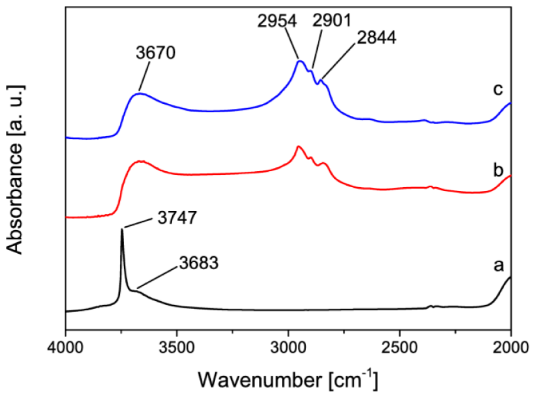


Figure 1. DRIFT-spectra of silica calcined at 600 °C (a), silica-supported MAO (b), and supported **1** (c).

(92.1 wt % of 1-hexene) of the catalyst is slightly reduced while the activity increased by about 35%. When the amount of *n*Oct$_3$Al present in the reactor was increased to 1.0 mmol, the catalyst's selectivity was completely lost. At the given conditions, **1** turns into a polymerization catalyst, producing 98.6 wt % of polyethylene and only a small trace of 1-hexene (1.3 wt %). A similar effect was observed when *i*Bu$_3$Al or Et$_3$Al were added to the reaction medium. However, already small quantities of *i*Bu$_3$Al, and especially Et$_3$Al, alter the catalyst's trimerization selectivity significantly leading to 82.5 and 42.3 wt % of 1-hexene, respectively. The effect of Me$_3$Al on the catalyst drastically differs in comparison to the other aluminum alkyls. For both high and low amounts of additional Me$_3$Al, the catalyst retains its high trimerization selectivity while the activity dramatically increased when compared to the reference experiment. The difference between Me$_3$Al and R$_3$Al (R = Et, *i*Bu, *n*-Oct) is striking. A possible explanation could be the presence of small amounts of aluminum hydrides, which might render **1** into a polymerization rather than a trimerization catalyst. However, control experiments did not support this hypothesis. Gambarotta et al. also demonstrated that very different chromium complexes can be obtained, which were either active as ethylene trimerization or polymerization catalysts, simply by altering the nature of the aluminum alkyl used.[45,46]

More detailed experiments concerning the effect of aluminum alkyls on the selectivity of the catalyst were conducted using *i*Bu$_3$Al. The ethylene oligomerization was conducted at different *i*Bu$_3$Al/MAO ratios and the effect on the trimerization selectivity is illustrated in Figure 2. Clearly, already the presence of small amounts of *i*Bu$_3$Al alters the selectivity of the catalyst. At an *i*Bu$_3$Al/MAO ratio of 0.04 (Al/Al) the selectivity toward 1-hexene production reduced to 82.5 wt %, which is 10 wt % lower than the selectivity of the catalyst in absence of additional *i*Bu$_3$Al. Further increasing the *i*Bu$_3$Al/MAO ratio leads to a rapid drop of selectivity and polyethylene rapidly becomes the main product. In all cases, the formed polyethylene was essentially linear (T_m = 135−140 °C) with a very high molecular weight and broad polydispersity ($M_w > 2 \times 10^6$ g·mol^{-1}; $Đ_M > 6$).

Supported Catalyst in the Presence of Different Scavengers. Analogous to the catalytic tests of the homogeneous catalyst, the immobilized catalyst was tested in the presence of different scavengers at two different concentrations (Table 4).

Without scavenger present, the catalyst exhibited a very low activity of 0.5 kg·mmol(Ti)$^{-1}$·h^{-1} while the selectivity toward trimerization was slightly lower (89.6 wt % 1-hexene) compared to the homogeneous system. Generally, when homogeneous scavengers were employed with the supported trimerization catalyst, the activities were around five to 10-fold lower compared to the corresponding homogeneous systems. When *n*Oct$_3$Al and *i*Bu$_3$Al are used as scavengers the activity depends on the concentration of the aluminum alkyls, leading to lower activities at higher concentration. In the presence of Me$_3$Al as scavenger, the catalysts activity was independent of the scavenger concentration. Compared to the homogeneous experiments a larger amount of branched decenes was formed (7.2−9.4 wt % versus 3.8−5.1 wt %), which can be explained by the high local concentration of 1-hexene within the pored of the catalyst particle. But why the amount of decenes is even 16.1−17.0 wt % when Et$_3$Al is used is not clear.

To exclude the effect of aluminum alkyls in the homogeneous phase, oligomerization experiments were con-

Table 2. Effect of Reaction Temperature and Pressure on Homogeneous 1[a]

entry	T (°C)	p (bar)	activity [kg(all)·mmol(Ti)$^{-1}$·h^{-1}]	wt % $C_6^=$ (%)[b]	wt % $C_{10}^=$ (%)[b]	wt % PE (%)
1	28	28	10.2	93.3	5.1	1.7
2	28	10	3.2	93.0	5.4	1.6
3	58	28	8.1	79.8	1.5	18.7
4	58	10	0.6	64.0	1.0	35.0

[a]Conditions: 1 μmol **1** for experiments at 28 bar $C_2^=$ and 2 μmol **1** for experiments at 10 bar $C_2^=$, Al_{MAO}/Ti = 2250, 28 bar $C_2^=$, 28 °C, 75 mL Isopar, 1 h. [b]Analyzed via GC-FID using *n*-decane as an internal standard.

DOI: 10.1021/acscatal.5b01359
ACS Catal. 2015, 5, 5068−5076

Table 3. Activity and Selectivity of Homogeneous 1 Activated by MAO and MAO/R_3Al Mixtures[a]

entry	R_3Al (amount)	activity [kg(all)·mmol(Ti)$^{-1}$·h^{-1}]	wt % $C_6^=$ (%)[b]	wt % $C_{10}^=$ (%)[b]	wt % PE (%)
1		10.2	93.3	5.1	1.6
2	*n*Oct$_3$Al (0.1 mmol)	13.8	92.1	4.1	3.8
3	*n*Oct$_3$Al (1.0 mmol)	8.0	1.3	< 0.1	98.6
4	*i*Bu$_3$Al (0.1 mmol)	13.0	82.5	4.0	13.5
5	*i*Bu$_3$Al (1.0 mmol)	7.0	10.9	0.5	88.6
6	Et$_3$Al (0.1 mmol)	8.6	42.3	2.0	55.7
7	Et$_3$Al (1.0 mmol)	7.7	1.4	<0.1	98.6
8	Me$_3$Al (0.1 mmol)	23.4	95.4	3.9	0.7
9	Me$_3$Al (1.0 mmol)	18.7	92.6	3.8	3.6

[a] Conditions: 1 μmol **1**, $Al_{MAO}/Ti = 2250$, 28 bar $C_2^=$, 28 °C, 75 mL Isopar, 1 h. [b] Analyzed via GC-FID using *n*-decane as an internal standard.

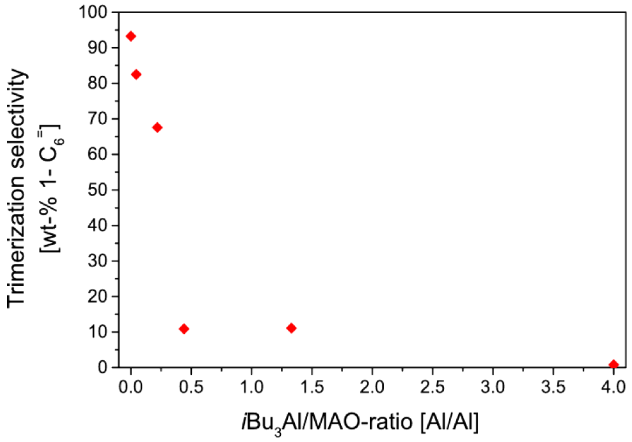


Figure 2. Selectivity toward 1-hexene as a function of *i*Bu$_3$Al/MAO ratio. Experimental conditions: 1 μmol **1**, $Al_{MAO}/Ti = 2250$, variable amount of *i*Bu$_3$Al, 28 bar $C_2^=$, 28 °C, 75 mL Isopar, 1 h.

ducted using supported scavengers. By immobilizing aluminum alkyls onto silica, they are physically separated from the catalyst and should not influence its activity. Employing silica-supported Et$_3$Al or *i*Bu$_3$Al as scavenger, the activity of immobilized **1** indeed increased significantly to 5.5–6.0 kg·mmol(Ti)$^{-1}$·h^{-1}. This indicates that homogeneous aluminum alkyls in general have a poisoning effect on silica-supported **1**. Using supported aluminum alkyls as scavenger, the selectivities toward the formation of 1-hexene, branched decenes and polyethylene were comparable to the values obtained with unsupported scavengers.

Besides the poisoning effect and the effect on selectivity, the choice of scavenger has a dramatic effect on the morphology of the polymeric side product, which is formed during the trimerization reaction. When *n*Oct$_3$Al or *i*Bu$_3$Al are used as scavengers, homogeneous polymer formation leading to reactor fouling was observed. It was argued that this might be the result of catalyst leaching (Scheme 3)—the highly soluble *n*Oct$_3$Al or *i*Bu$_3$Al might be soluble enough to form homogeneous cationic species, although at this time there is no proof for this assumption. Using Et$_3$Al, Me$_3$Al or silica-supported scavengers, no reactor fouling was observed and the obtained polyethylene formed discrete particles, which could easily be removed from the reactor. This effect is best illustrated by scanning electron microscope images of the polymer produced (Figure 3).

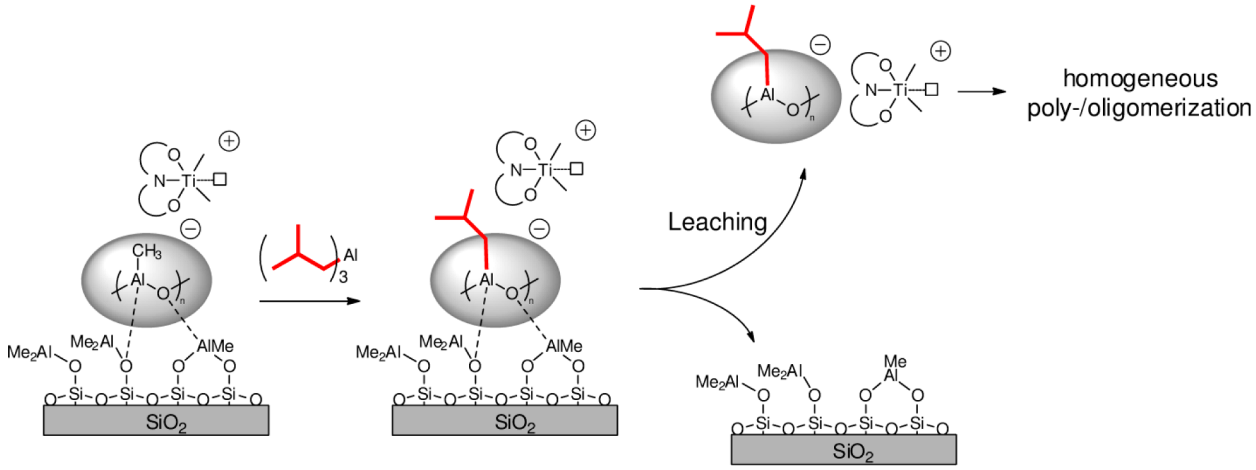
Comparing the homogeneous and silica-supported trimerization catalyst is difficult. The striking difference of the effect of aluminum alkyls in the reaction medium is obvious. While the homogeneous system switches from selective ethylene trimerization to polymerization in the presence of aluminum alkyls, the supported catalyst retains its selectivity. Generally, the activity of the supported system was lower than the activity of the homogeneous catalyst activated by MAO. This can partly be explained by poisoning of the active species by the aluminum alkyls when homogeneous scavengers are employed. The low activity using supported scavengers must result from different origins. The relatively small amount of polyethylene formed during the reaction could for example result in poor catalyst fragmentation and consequently clogging of the pores, hampering ethylene diffusion to the active sites. Alternatively, the lower activity might result from a lower MAO/catalyst ratio in the supported system or from the fact that **1** is being activated during the supportation and the active catalyst might have limited thermal stability, especially in the absence of ethylene.

Table 4. Activity and Selectivity of Supported 1 in the Presence of Different Aluminum Alkyls[a]

entry	R_3Al (amount)	activity [kg(all)·mmol(Ti)$^{-1}$·h^{-1}]	wt % $C_6^=$ (%)[b]	wt % $C_{10}^=$ (%)[b]	wt % PE (%)	fouling
1		0.5	89.6	8.3	2.1	none
2	*n*Oct$_3$Al (0.1 mmol)	2.1	90.0	9.4	0.6	medium
3	*n*Oct$_3$Al (1.0 mmol)	1.3	87.9	9.0	3.1	medium
4	*i*Bu$_3$Al (0.1 mmol)	3.0	91.1	7.2	1.7	severe
5	*i*Bu$_3$Al (1.0 mmol)	1.8	89.2	8.4	2.4	severe
6	Et$_3$Al (0.1 mmol)	1.3	79.4	17.0	3.6	none
7	Et$_3$Al (1.0 mmol)	1.2	78.5	16.1	5.4	none
8	Me$_3$Al (0.1 mmol)	2.1	92.1	7.1	0.8	none
9	Me$_3$Al (1.0 mmol)	2.1	91.6	6.6	1.8	none
10	Et$_3$Al/SiO$_2$ (615 mg)	6.0	89.9	8.7	1.4	none
11	*i*Bu$_3$Al/SiO$_2$ (615 mg)	5.5	90.9	8.0	1.1	none

[a] Conditions: 100 mg supported **1**, 28 bar $C_2^=$, 28 °C, 75 mL Isopar, 1 h. [b] Analyzed via GC-FID using *n*-decane as an internal standard.

Scheme 3. Catalyst Leaching Caused by Solubilizing the Cocatalyst by Alkyl Exchange with the Scavenger



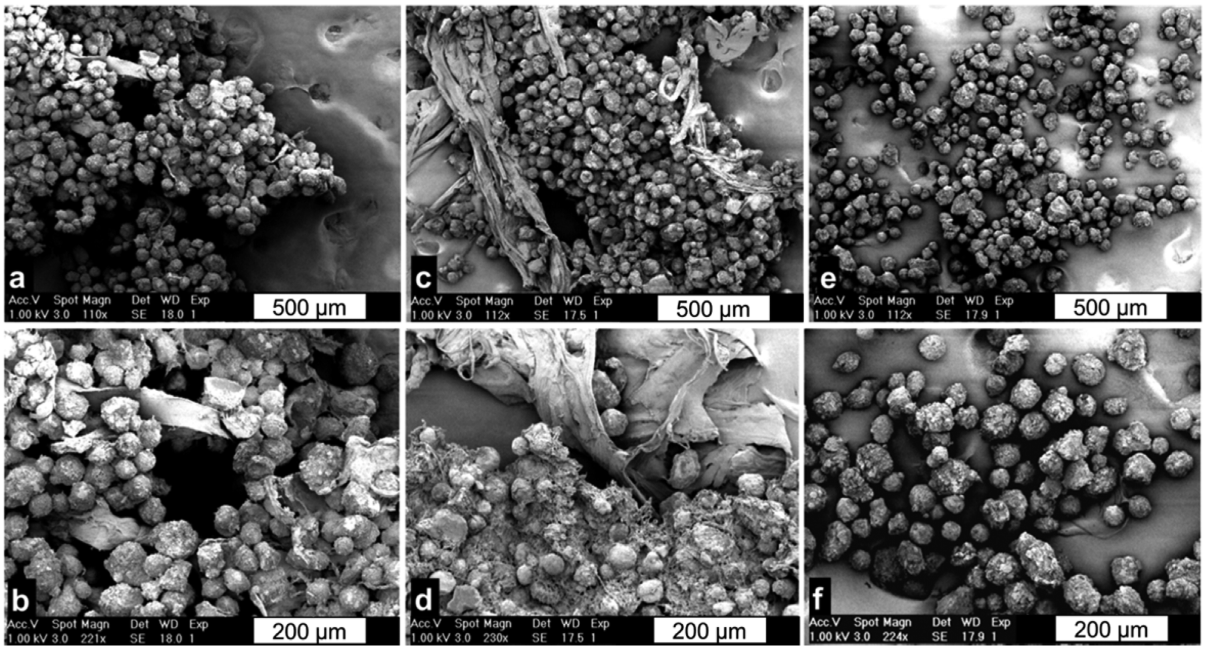


Figure 3. Scanning electron microscope images of polymer produced by supported **1** in the presence of different scavengers (0.1 mmol R_3Al): (a, b) *n*Oct_3Al, (c, d) *i*Bu_3Al, and (e, f) Me_3Al.

Table 5. Activity and Selectivity of 1 after Contacting the Catalyst Precursor with Aluminum Alkyls[a]

entry	catalyst premixed with[b]	co-cat./scavenger in reactor	activity [kg(all)·mmol(Ti)$^{-1}$·h^{-1}]	wt % $C_6^=$ (%)[c]	wt % $C_{10}^=$ (%)[c]	wt % PE (%)
1		MAO (2250 Al/Ti)	10.2	93.3	5.1	1.7
2	MAO (750 Al/Ti)	MAO (1500 Al/Ti)	9.8	92.8	5.1	2.1
3	MAO (2250 Al/Ti)	Et_3Al (100 Al/Ti)	20.5	93.0	3.5	3.5
4	MAO (2250 Al/Ti)	Me_3Al (100 Al/Ti)	19.9	95.1	3.9	1.0
5	Et_3Al (100 Al/Ti)	MAO (2250 Al/Ti)	5.8	1.5	<0.1	98.5
6	Me_3Al (100 Al/Ti)	MAO (2250 Al/Ti)	2.6	13.6	0.7	85.7

[a] Conditions: 1 µmol **1**, 28 bar $C_2^=$, 28 °C, 75 mL Isopar, 1 h. [b] Catalyst was contacted with corresponding aluminum alkyl at room temperature for 1 h. [c] Analyzed via GC-FID using *n*-decane as an internal standard.

Homogeneous Catalyst-Activated Species in the Presence of Aluminum Alkyls. To elucidate whether this difference in activation has an influence on the activity and selectivity, homogeneous experiments were conducted with **1** being contacted with MAO before being injected into the reactor (Table 5). Furthermore, complementary experiments were conducted in which **1** was contacted with aluminum alkyls before being injected into the reactor containing MAO. Precontacting **1** with MAO changed neither the activity nor the selectivity of the homogeneous catalyst when compared to the homogeneous reference experiment (Table 5), indicating that with sufficient MAO present the activated catalyst is relatively stable.

When the MAO-preactivated catalyst was injected into an autoclave charged with the aluminum alkyls (Table 5, entries 3 and 4), the activity increased while the selectivity toward 1-hexene production remained unchanged, similar as when **1** was activated with a mixture of Me_3Al and MAO (Table 3). Most likely, the added aluminum alkyls effectively scavenges impurities. By treating **1** with aluminum alkyls (Table 5, entries 5 and 6) prior to contacting with MAO, surprisingly, the selectivity switched to polymerization. In comparison to the activation by R_3Al/MAO mixtures as described above, the effect is more pronounced when **1** is contacted first with the aluminum alkyl alone—the activation of **1** with a mixture of Et_3Al/MAO led to the formation of 42.3 wt % 1-hexene and 55.7 wt % polyethylene. Precontacting **1** with the same amount of Et_3Al in the absence of MAO led to a complete switch of selectivity to polymerization (98.5 wt % polyethylene). Interestingly, also the reaction of **1** with Me_3Al in the absence of MAO resulted in a loss of selectivity for trimerization. This is surprising, since Me_3Al is an ingredient of MAO and the addition of Me_3Al to the cocatalyst resulted in a higher activity and good trimerization selectivity (Table 3, entries 8 and 9).

To elucidate the fate of **1** in the presence of MAO and/or aluminum alkyls, NMR studies were conducted (Figure 4).

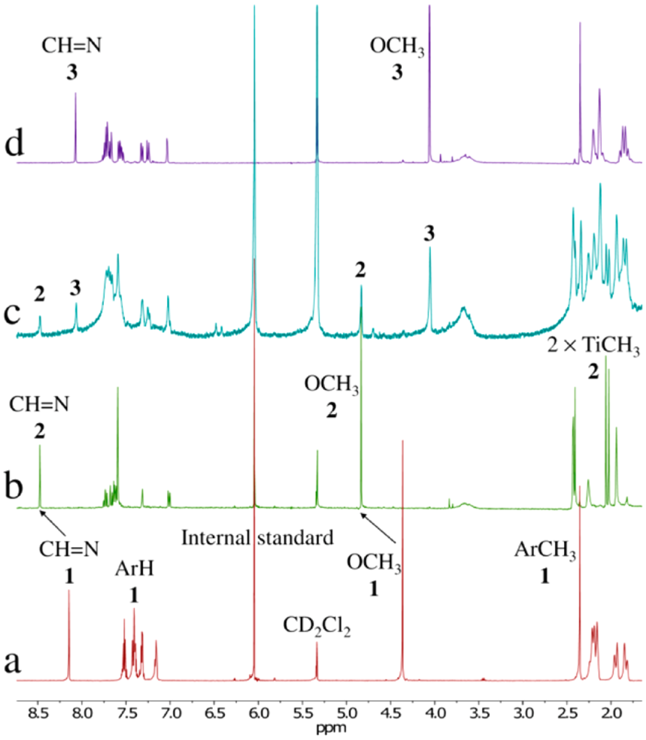


Figure 4. ^1H NMR of (a) **1**, (b) **1** reacted with a mixture of Me_3Al and DMAO (Me_3Al:DMAO = 1:10; Al/Ti = 100) followed by Me_3Al (Al/Ti = 10), (c) **1** reacted with Me_3Al (Al/Ti = 10) followed by DMAO (Al/Ti = 100), (d) the free phenoxy-imine ligand reacted with Me_3Al followed by DMAO. The DMAO Al–Me resonances are not shown (1.5–1.9 ppm).

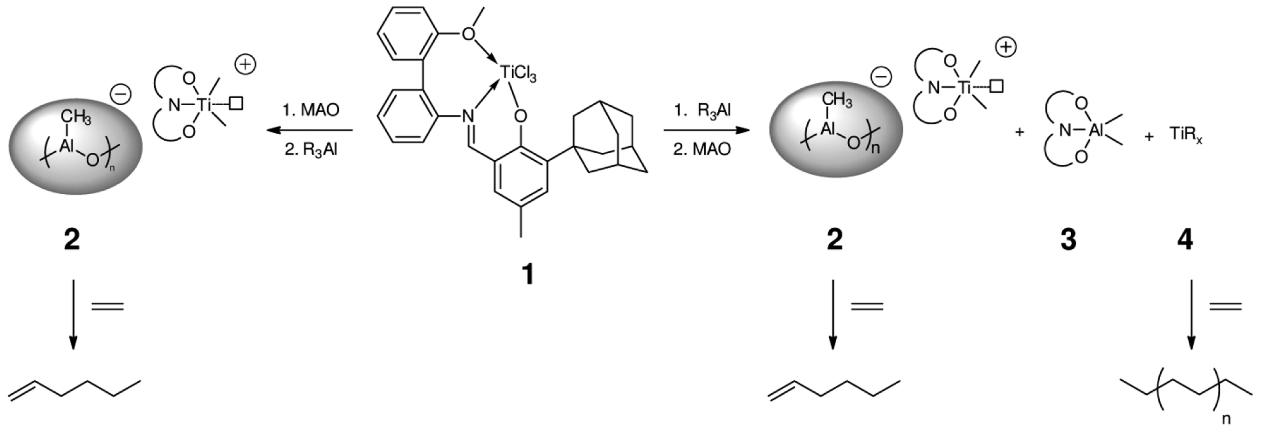
Since the solvent signal of commonly employed MAO solutions would disturb the spectroscopic investigation, NMR experiments were conducted using solvent dried MAO (DMAO). Similar to the oligomerization reactions described above (Table 5) **1** was either reacted first with a mixture of Me_3Al and DMAO (Me_3Al:DMAO = 1:10) followed by additional Me_3Al or first Me_3Al followed by DMAO. The reaction of **1** (Figure 4a) with the mixture of Me_3Al and DMAO (Al/Ti = 100) followed by Me_3Al (Al/Ti = 10) (Figure 4b) proceeds cleanly and yields the cationic dimethylated species **2**. The characteristic peaks of the imine proton and the methoxy group shift upfield and the comparison of their integral values with the internal standard (tetrachloroethane) indicate a quantitative reaction. The reaction of **1** with Me_3Al (Al/Ti = 10), followed by DMAO (Al/Ti = 100) results in the formation of two species (Figure 4c). Besides the characteristic signals of **2**, additional peaks for a second methoxy and imine group are visible and assigned to species **3**. Species **3** was identified as the aluminum complex of the ligand by reaction of the free ligand with Me_3Al and DMAO (Figure 4d). It should be noted that a similar ligand exchange between precatalyst **1** and MeMgBr was observed by Sattler et al.[47] The ligand transfer from titanium to aluminum results in the formation of ligand-free titanium alkyl species. The latter can be compared to a traditional Ziegler–Natta catalyst for α-olefin polymerization, which results from the reaction of $TiCl_4$ with aluminum alkyls (e.g., Et_3Al). Based on the integral ratio between the imine protons and the internal standard the relative amount of **1** undergoing activation to **2** calculates to be 15%, while 33% is undergoing ligand transfer to aluminum to form **3**. This means that about 52% of the initially present precatalysts are not detected by NMR-spectroscopy (whereas a clear solution was obtained), which suggests that paramagnetic low-valent phenoxy-imine titanium species have been formed. The reduction of precatalyst **1** by aluminum alkyls was studied in detail by NMR and EPR spectroscopy by Soshnikov et al.[48] Similar to our results, the authors show that about 20–70% of **1** was reduced to Ti(III) complexes when reacted with aluminum alkyls. Furthermore, the cationic Ti(III)-complex resulting from the subsequent reaction of **1** with *i*Bu_3Al and MAO is assumed to be active in ethylene polymerization. Hence, both the ligand transfer to aluminum and the reduction of the titanium complex are likely to be responsible for polymer formation.

The conclusions from homogeneous catalyst testing and NMR experiments are graphically summarized in Scheme 4. The reaction of **1** with MAO or a mixture of MAO and Me_3Al results in the formation of the cationic dimethylated species **2**. Upon contact with ethylene, **2** undergoes reduction to the actual active Ti(II) species as described for related titanium-based trimerization systems.[47–49] The alkylation of **1** in the absence of MAO as a cationization agent results in an unstable titanium trialkyl species, which partially undergoes ligand transfer from titanium to aluminum and reduction to lower valency. The hereby formed "ligand-free" titanium alkyls and reduced titanium species (**4**) result in an increase of polymer formation and a decrease of selectivity toward the production of 1-hexene.

■ CONCLUSIONS

The phenoxy-imine titanium catalyst for ethylene trimerization was successfully immobilized on MAO-pretreated silica and its catalytic behavior was compared with that of the corresponding homogeneous system. Both the homogeneous and heterogeneous systems are strongly affected by aluminum alkyls, which are commonly employed as scavengers in processes using heterogeneous olefin polymerization catalysts. In general, silica-supported **1** was found to be poisoned by aluminum alkyls present in the homogeneous reaction medium. Furthermore, in the presence of *n*Oct_3Al and *i*Bu_3Al as scavengers, reactor

Scheme 4. Effect of Aluminum Alkyls on Precatalyst and Activated Catalyst



fouling by homogeneous polymer formation was observed as a consequence of catalyst leaching. In the presence of Me_3Al and Et_3Al as scavenger, the polymer formed exclusively inside the particle and hence reactor fouling was prevented. It was demonstrated that applying silica-supported scavengers prevented the poisoning effect of aluminum alkyls on the immobilized catalysts, leading to high trimerization activity while preventing reactor fouling.

The corresponding homogeneous system exhibited a far different reactivity toward aluminum alkyls. Activation of the catalyst by a mixture of MAO and various aluminum alkyls (with exception of Me_3Al) leads to a switch of selectivity from ethylene trimerization to polymerization. Spectroscopic investigations indicate that this effect can be attributed to ligand transfer from **1** to aluminum. The MAO-activated catalyst, however, does not suffer from ligand transfer.

■ EXPERIMENTAL SECTION

Materials and General Considerations. All reactions and modifications of air and moisture sensitive compounds were conducted under inert gas atmosphere (nitrogen or argon) using standard Schlenk and glovebox techniques. Silica (Sylopol 948, particle diameter ~50 μm) was kindly provided by Grace Davison and calcined at 600 °C in a nitrogen stream before use. Neat trimethylaluminum, triethylaluminum, triisobutylaluminum and a 25 wt % solution of tri-*n*-octylaluminum in hexanes were purchased from Sigma-Aldrich and used without further purification. All experiments have been performed with fresh and cooled bottles of aluminum alkyls and the aluminum alkyls were checked by NMR on the presence of hydrides. Isopar E (isomeric mixture of octanes and nonanes, Brentag), toluene (technical, Biosolve), and ethylene (purity 4.5, Linde) were deoxygenized and dried by passing them subsequently through columns containing BTS-catalyst and molecular sieves (3 Å). Dichloromethane-d_2 (Sigma-Aldrich) was dried over calcium hydride before use. Samples for NMR spectroscopy were prepared in a glovebox and sealed in Young-tap containing NMR tubes. Methyl aluminoxane (30 wt % in toluene, Chemtura) was used without modifications. Depleted MAO (DMAO) was prepared from MAO solution (10 wt % in toluene, Sigma-Aldrich) by evaporation of solvent and free Me_3Al in vacuum at 80 °C for 2 days. The FI precatalyst (**1**) was prepared according to literature procedures.[7] Elemental analysis was performed at Mikroanalytisches Laboratorium Kolbe (Mühlheim, Germany).

Characterization. NMR spectroscopy was performed on a Varian Mercury 400 MHz spectrometer. The residual proton resonance of the NMR solvent was used as a reference for the reported chemical shifts. Gas chromatography was conducted on a Varian 450-GC equipped with a C18 factor four column (30 m × 0.25 mm) and an FID detector. Samples of the reaction mixture were diluted in ethanol before measurement. For the quantification of the produced 1-hexene and decenes calibration curves of 1-hexene and 1-decen against the internal standard (*n*-decane) were used. Diffuse reflectance infrared spectroscopy (DRIFT) was performed on a Varian 670 spectrometer using an Alltech DRIFT assembly. Samples were placed in an open aluminum cup for measurements and 50 scans with a resolution of 4 cm^{-1} were recorded. The spectrum of an empty sample cup was used as a background. Nitrogen physisorption was performed on a Micrometrics Tristar II at −198 °C. The adsorption isotherm was analyzed via the Barrett−Joyner−Halenda method (BJH method) to obtain the pore surface area, pore diameter, and pore volume.

Preparation of Silica-Supported Methyl Aluminoxane (MAO/SiO_2). MAO (15 mL, 30 wt % in toluene) was diluted with toluene (20 mL) and added to calcined silica (10 g) under manual agitation. Subsequently, the slurry was heated to 80 °C and occasionally agitated. After 2 h the solvent was removed under nitrogen flow at 80 °C to obtain the silica-supported MAO as a free-flowing powder.

Immobilization of 1 on MAO/SiO_2. A solution of **1** (18.1 mg, 0.03 mmol) in toluene (13.8 mL) was added to silica-supported MAO (1.5 g) at room temperature. The thereby obtained slurry was heated to 50 °C for 1 h during which time it was resuspended by shaking every 15−20 min. After cooling to room temperature the supported catalyst was filtered and washed with toluene (5 × 15 mL), light petroleum ether (2 × 15 mL) and dried in vacuum to obtain a yellow, free-flowing powder. The immobilized catalyst was immediately used in ethylene oligomerization experiments since prolonged storage of the catalyst led to deactivation.

Immobilization of Aluminum Alkyls on Silica (Et_3Al/SiO_2 and iBu_3Al/SiO_2). Solutions of aluminum alkyls in toluene (~30 wt %, 14 mL) were added dropwise to slurries of silica (10 g) in toluene (100 mL) under mechanical agitation. After 3 h the solids were allowed to settle and the supernatants were carefully decanted. The silica-supported scavengers were washed with toluene (5 × 100 mL) and subsequently dried in vacuum.

Typical Ethylene Oligomerization Procedure. Catalytic tests were conducted in a 125 mL stainless steel Premex-reactor equipped with a mechanical stirrer, a bottom valve for sampling of the liquid phase, and a custom-made injection system allowing catalyst injections under high ethylene pressure. The reactor was dried in four nitrogen/vacuum cycles at 130 °C before cooling it to the reaction temperature of 28 °C. The reactor was charged with solvent (Isopar E, 50 mL), the scavenger plus the internal standard (in 10 mL Isopar E). Subsequently the reactor was pressurized with ethylene ($p(C_2^=)$ = 28 bar). After saturating the reaction mixture with ethylene for 1 h, the catalyst (in 15 mL Isopar E) was injected into the reactor. After a reaction time of 1 h, the ethylene supply was stopped and a sample of the reaction mixture was collected in a steel sample vessel via the bottom valve of the reactor. The steel sample vessel was cooled to −30 °C before depressurizing it and the thus obtained liquid sample was immediately analyzed by GC-FID. Directly after drawing the sample from the reaction mixture, the reactor was depressured and the remaining reaction mixture quenched with a mixture of ethanol (150 mL) and diluted aqueous hydrochloric acid (50 mL, 10 wt %). After stirring for 1 h the remaining solid products were filtered, washed with ethanol, and dried in a vacuum oven at 70 °C. Each experiment was conducted at least twice to ensure the reproducibility of the corresponding outcome.

NMR Studies. A 24 mM stock solution of **1** (22 mg, 0.036 mmol) was prepared in dichloromethane-d_2 (1.5 mL) containing tetrachloroethane as internal standard. Aliquots of the stock solution were employed in the following NMR experiment. ^{1}H NMR (400 MHz, dichloromethane-d_2, 298 K) **1**: δ 8.15 (s, 1H, N═CH), 7.55−7.49 (m, 2H, ArH), 7.43−7.38 (m, 4H, ArH), 7.33−7.30 (m, 2H, ArH), 7.17−7.14 (m, 2H, ArH), 4.36 (s, 3H, OCH_3), 2.35 (s, 3H, $ArCH_3$), 2.24−2.16 (m, 9H, 3 × CH and 3 × CH_2 adamantyl), 1.89 (dd, J_1 = 45 Hz, J_2 = 12 Hz, 6H, 3 × CH_2 adamantyl). The integral ratio between the imine proton of **1** and the internal standard was 0.4.

Reaction of 1 with Me_3Al/DMAO. To the above-mentioned stock solution of **1** (0.3 mL, 7.2 μmol) was added a solution of Me_3Al and DMAO (Me_3Al:DMAO = 1:10, 1.6 M total Al) in dichloromethane-d_2 (0.5 mL, 0.800 mmol). The reaction caused an immediate color change from orange to yellow. ^{1}H NMR (400 MHz, dichloromethane-d_2, 298 K) **2**: δ 8.48 (s, 1H, N═CH), 7.76−7.58 (m, 8H, ArH), 7.32 (d, J = 1.2 Hz, 1H, ArH), 7.01 (dd, J_1 = 7.8 Hz, J_2 = 1.0 Hz, 1H, ArH), 4.83 (s, 3H, OCH_3), 2.43 (m, 6H, 3 × CH_2 adamantyl), 2.41 (s, 3H, $ArCH_3$), 2.26 (m, 3H, 3 × CH adamantyl), 2.06 (s, 3H, $TiCH_3$), 2.03 (s, 3H, $TiCH_3$), 1.94 (m, 6H, 3 × CH_2 adamantyl). The integral ratio between the imine proton and the internal standard was 0.4 indicating quantitative formation of the methylated cationic species of the catalyst $[LTiMe_2]^+[MeMAO]^-$ (**2**).

Reaction of 1 with Me_3Al and Subsequent Reaction with DMAO. To the stock-solution of **1** (0.3 mL, 7.2 μmol Ti) was added a 0.15 M solution of Me_3Al in dichloromethane-d_2 (0.5 mL, 0.075 mmol) upon which the color of the solution changed from orange to dark brown. After 10 min, DMAO (21 mg, 0.362 mmol) in dichloromethane-d_2 (0.5 mL) was added. The ^{1}H NMR spectrum showed the formation of **2** together with a second species **3**, which could be identified as the product resulting from ligand transfer to aluminum ($LAlMe_2$, see below). The integral ratio of the imine protons and the internal standard were 0.06 and 0.13 for **2** and **3**, respectively. The lower than expected amount of **2** plus **3** suggests the additional formation of one or more paramagnetic compounds.

Reaction of Phenoxy-Imine Ligand with Me_3Al and DMAO. The free phenoxy-imine ligand (10 mg, 0.022 mmol) was reacted with Me_3Al (16 mg, 0.222 mmol) in dichloromethane-d_2 (1 mL). After a reaction time of 10 min DMAO (128 mg, 2.207 mmol) was added to the solution. The reaction yielded the aluminum complex **3** ($LAlMe_2$). ^{1}H NMR (400 MHz, dichloromethane-d_2, 298 K) **3**: δ 8.07 (s, 1H, N═CH), 7.77−7.66 (m, 5H, ArH), 7.59−753 (m, 2 H, ArH), 7.32 (m, 1H, ArH), 7.25 (m, 1H, ArH), 7.03 (d, J = 2.0 Hz, 1H, ArH), 4.06 (s, 3H, OCH_3), 2.35 (s, 3H, Ar−CH_3), 2.20−2.05 (m, 9H, 3 × CH and 3 × CH_2 adamantyl), 1.85 (q, 6H, J = 12.3 Hz, 3 × CH_2 adamantyl).

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is part of the research program of the Dutch Polymer Institute (DPI) under the project no. 706.

ABBREVIATIONS

MAO, methyl aluminoxane; DMAO, depleted methyl aluminoxane; Me_3Al, trimethylaluminum; Et_3Al, triethylaluminum; *i*Bu_3Al, triisobutylaluminum; *n*Oct_3Al, trioctylaluminum; BJH, Barrett− Joyner−Halenda; DRIFT, diffuse reflectance infrared spectroscopy; NMR, nuclear magnetic resonance

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