

Linked cyclopentadienyl-amido titanium catalysts supported on pyridylethylsilane-modified silica for heterogeneous ethylene homo- and copolymerization

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Abstract

Linked cyclopentadienyl-amido titanium dimethyl and dichloro complexes, $\text{Ti}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\text{X}_2$ ($\text{X} = \text{Me}$, Cl), were reacted with trityl tetrakis(pentafluorophenyl)borate (TB), $\text{Ph}_3\text{C}^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, and methylaluminoxane (MAO), followed by treatment with toluene suspension of pyridylethylsilane-modified silica, to give two new supported-type titanium catalysts, PySTiTB and PySTiMAO. PySTiTB polymerized ethylene in the presence of triisobutylaluminum (TIBA) in hexane at 60 °C and 5 bar with slightly higher activity than the corresponding homogeneous system under the same conditions. PySTiMAO showed relatively high activity even without any use of alkylaluminum compound. The activity could be improved to reach the value comparable with that of the corresponding homogeneous system, when TIBA and modified MAO (MMAO) were employed as external aluminum compounds. Polyethylenes obtained with PySTiTB were found to have molecular weights (M_w) slightly above 10^6 and narrow molecular weight distributions (MWDs), $M_w/M_n = 1.8\text{--}3.0$. Polyethylenes obtained with PySTiMAO have M_w ranging from 1.5×10^5 to 1.2×10^6 and narrow MWDs when combined with TIBA, but very broad MWDs ($M_w/M_n = 5.0\text{--}13.4$), when MMAO was used instead of TIBA. Both new supported titanium catalysts also showed modest activities in random copolymerization of ethylene with 1-octene. The present supported catalysts produced copolymers with lower 1-octene contents compared to the corresponding homogeneous systems. PySTiMAO, when combined with MMAO, gave copolymers with highest 1-octene contents, and the MWDs of the resulting copolymers were found to be in a wide range varying from 3.0 up to as broad as 25.

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1. Introduction

The heterogenization of metallocenes or single-site catalysts is successfully performed by three methods: (i) immobilization of methylaluminoxane (MAO)

[1–5], borane- or borate-based activators [6–11] on silica or other inorganic and polymeric supports, followed by the reaction with metal complexes; (ii) immobilization of metal complexes either through covalently binding of the ligands or the metal centers on the supports first, then reacting with MAO to form the active catalysts [12–18]; (iii) direct immobilization of the activated catalysts formed after the contact of metal complexes with MAO on the supports [19–22].

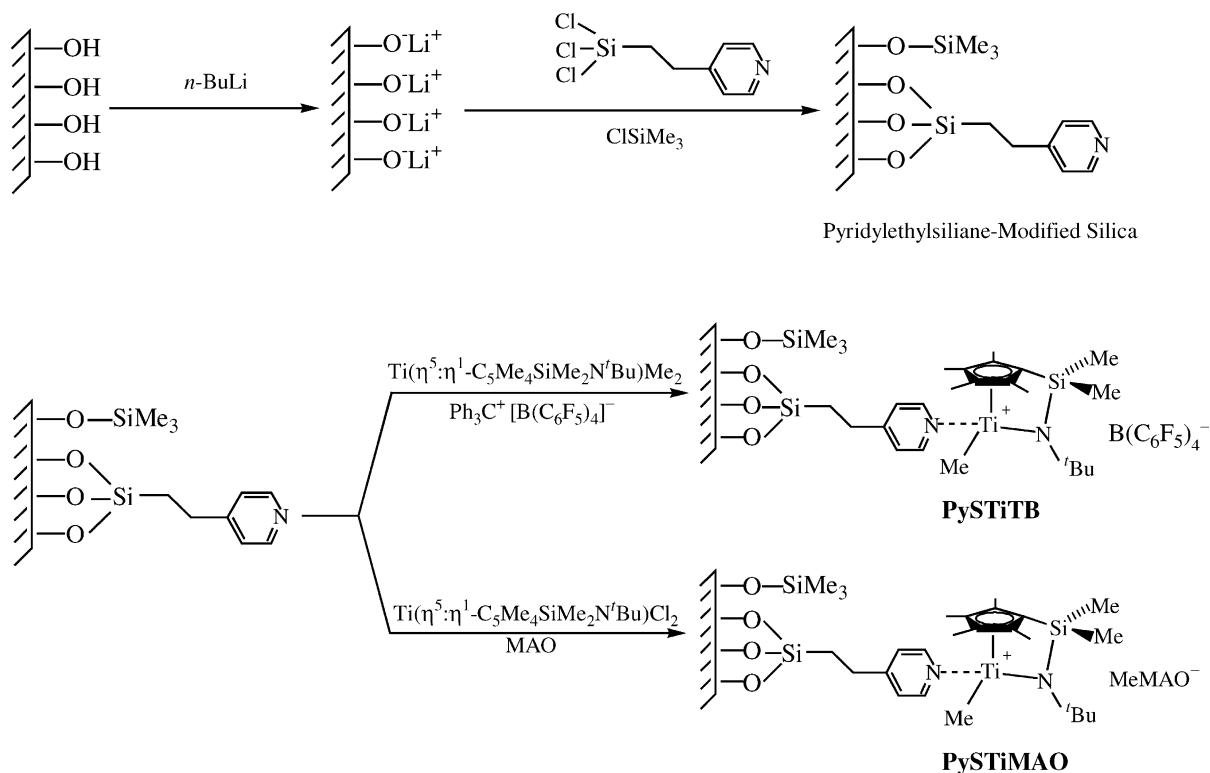
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The third method is considered to be more efficient and convenient for the catalyst preparation process due to several advantages such as maximizing the number of active sites, producing highly active supported catalysts at much lower Al/metal ratios, and reducing the cost and time for the catalyst preparation. Among all kinds of the supports, silica is the most widely used because it has a high surface area, porosity, and good mechanical properties. There are also examples of works on immobilization of metallocene/MAO by the third method on polymeric supports such as reversible cross-linked polystyrene [23] or latex particle [24]. The idea here is to bind the active metal centers onto the support surface through weak coordination to Lewis basic functional groups of the supports.

The application of the third method with single-site catalysts and borane- or borate-based activators is more problematic than MAO-based systems, because these cationic catalyst systems are much more sensitive to impurities and also to the surface hydroxyl

groups of the supports like silica and alumina, which normally lead to fast deactivation of the catalysts. However, the treatment of the silica or alumina with common alkyl aluminum compounds before the contact with metallocene dimethyl complex/borate activator was found to be one of the efficient ways to solve the problem [25,26]. The use of polymeric supports is another alternative. For instance, cross-linked poly(4-vinylpyridine) as support for the immobilization of bis(cyclopentadienyl)zirconium dimethyl/trityl tetrakis(pentafluorophenyl)borate has been shown to give supported catalyst with higher activity than the corresponding homogeneous system. The catalyst could be kept as hexane suspension for as long as 1 month without any deactivation observed [27].

Although, there have been already a large number of publications on the immobilization of metallocenes/boron- or borate-based activators by the third method on inorganic and polymeric supports, still only few reports on the application of this method to



Scheme 1. Preparation method of new supported-type linked cyclopentadienyl-amido titanium catalysts.

linked cyclopentadienyl-amido titanium catalysts, so-called constrained-geometry catalysts, a new family of highly active homogeneous Ziegler-type catalysts for ethylene homopolymerization and copolymerization with α -olefins, were disclosed. The heterogenization of these CGC titanium catalysts is aiming at improving the morphology of the polymer products and solving the reactor-fouling problem. By combining the advantages of using silica material and poly(4-vinylpyridine) previously described, we report here the work on the immobilization by the third method of (i) linked cyclopentadienyl-amido titanium dimethyl/trityl tetrakis(pentafluorophenyl)borate, $\text{Ti}(\eta^5\text{:}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\text{Me}_2/\text{Ph}_3\text{C}^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, and of (ii) linked cyclopentadienyl-amido titanium dichloro complex/MAO, $\text{Ti}(\eta^5\text{:}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\text{Cl}_2/\text{MAO}$, on pyridylethylsilane-modified silica, called PySTiTB and PySTiMAO, respectively (see Scheme 1). The catalytic behavior of these two new supported titanium catalysts in ethylene homo- and copolymerization as well as the properties and morphology of the resulting polymers have been investigated.

2. Experimental

2.1. Materials

All experiments were performed under argon in a glove-box or by standard Schlenk techniques. All solvents were purified by standard distillation methods. Linked cyclopentadienyl-amido titanium dimethyl complex (CGCTiMe₂), $\text{Ti}(\eta^5\text{:}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\text{Me}_2$, and dichloro complex (CGCTiCl₂), $\text{Ti}(\eta^5\text{:}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\text{Cl}_2$, were synthesized by our group [28–30]. Trityl tetrakis(pentafluorophenyl)borate (TB), $\text{Ph}_3\text{C}^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, was donated by Ticona GmbH. Trimethylaluminum (TMA), triethylaluminum (TEA), triisobutylaluminum (TIBA), methylaluminoxane (MAO) 10 wt.% in toluene solution and modified methylaluminoxane (MMAO) 10 wt.% in heptane solution were purchased from Witco GmbH and used as received. 4-[2-(Trichlorosilyl)ethyl]pyridine ($\text{Cl}_3\text{SiC}_2\text{H}_4\text{C}_5\text{H}_4\text{N}$) 25 wt.% in toluene and chlorotrimethylsilane (ClSiMe_3) were purchased from ABCR GmbH & Co. KG and ACROS Organics, respectively and used as received. 1-Octene from

ACROS Organics was purified by vacuum distillation over CaH_2 . Highly pure grade ethylene from Linde AG and other chemical reagents were used without any further purification. Sylopol[®] 948 silica, donated by GRACE GmbH (300 m²/g surface area, 20 nm pore diameter, 50 μm particle size) was calcined under air atmosphere at 500 °C for 5 h and dried under vacuum at 200 °C for 6 h prior to use. The silanol content ($\equiv\text{Si-OH}$) of the calcined silica material was determined by thermogravimetric method [31] and estimated to be 1.18 mmol/g.

2.2. Preparation of pyridylethylsilane-modified silica

To a toluene suspension of 10 g (silanol content = 11.8 mmol) calcined silica at 0 °C, was added dropwise 1.4 eq. of *n*-BuLi in hexane solution. The suspension was then warmed up to room temperature and heated to 60 °C and stirred for 5 h, followed by decantation, washing with toluene and hexane several times, and drying in vacuo to give a lithiated silica. The lithium content was determined by titration using 0.1 M HCl (aqueous), and found to be 1.20 mmol/g. Next, 4.5 g (lithium content = 5.4 mmol) of lithiated silica was suspended in toluene, and 1.5 eq. of 25 wt.% toluene solution of $\text{Cl}_3\text{SiC}_2\text{H}_4\text{C}_5\text{H}_4\text{N}$ was added, and the suspension was then heated to 60 °C and stirred for 3 h. After cooling down to room temperature, 1.5 eq. of ClSiMe_3 was added in order to further reduce silanol groups of silica as many as possible, and the suspension was kept stirring at room temperature overnight, followed by decantation, washing with toluene, ether and hexane several times, and drying in vacuo. The pyridylethylsilane-modified silica was finally obtained as off-white solid particles. The elemental analysis of CHN was found to be C, 7.91; H, 2.34; N, 0.89 %. From this result, the N content, which represents the pyridine content, could be estimated to be 0.64 mmol/g.

2.3. Preparation of supported

$\text{Ti}(\eta^5\text{:}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\text{Me}_2/\text{Ph}_3\text{C}^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (PySTiTB)

To 20 ml toluene solution of 0.35 g (0.38 mmol) $\text{Ph}_3\text{C}^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, was added 15 ml toluene solution of 0.124 g (0.38 mmol) $\text{Ti}(\eta^5\text{:}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})$

Me₂. The reaction mixture was stirred at room temperature for 30 min. Then, 0.6 g (N content = 0.38 mmol) of pyridylethylsilane-modified silica was added via a funnel, and the suspension was stirred at room temperature overnight. After decantation, washing with hexane several times, and drying in vacuo, the new supported CGCTiMe₂/TB catalyst (PySTiTB) was obtained as yellow solid particles. The Ti and B contents were determined by high-resolution-inductively coupled plasma-mass-spectrometry (HR-ICP-MS) and found to be 0.186 and 0.244 mmol/g, respectively.

2.4. Preparation of supported

Ti(η⁵:η¹-C₅Me₄SiMe₂N^tBu)Cl₂/MAO (PySTiMAO)

To 28.5 ml (57 mmol of Al) of 10 wt.% MAO solution in toluene, was added 15 ml toluene solution of 0.140 g (0.38 mmol) Ti(η⁵:η¹-C₅Me₄SiMe₂N^tBu)Cl₂. The reaction mixture was stirred at room temperature for 30 min. Then, 0.6 g (N content = 0.38 mmol) of pyridylethylsilane-modified silica was added via a funnel, and the suspension was stirred at room temperature overnight. After decantation, washing with hexane several times, and drying in vacuo, the new supported CGCTiCl₂/MAO catalyst (PySTiMAO) was obtained as pale yellow solid particles. The Ti and Al contents were determined by HR-ICP-MS and found to be 0.043 and 4.67 mmol/g, respectively.

2.5. Ethylene polymerization

Ethylene polymerization was carried out in hexane at 60 °C and 5 bar ethylene pressure in a 100 ml Büchi glass reactor equipped with a magnetic stirrer. In the glove box, the required amounts of hexane, alkylaluminum compounds or MMAO, supported catalysts (PySTiTB or PySTiMAO) were respectively added into the reactor. Then, the reactor was immediately transferred out of the glove box without aging the catalyst system and placed in an oil bath on a magnetic stirrer to perform polymerization. Polymerization was started after introducing ethylene into the evacuated reactor, and the pressure was controlled by the pressure regulator and kept constant at 5 bar throughout the polymerization time. Termination was performed by venting the reactor, adding 1 ml methanol, and the polymerization product mixture was then precipitated in acidified methanol. The obtained polymer was

filtered and washed with methanol several times, followed by drying at 70 °C in air to a constant weight.

2.6. Ethylene copolymerization with 1-octene

Ethylene copolymerization was carried out in hexane at 60 °C and 5 bar ethylene pressure in a 200 ml Büchi glass reactor equipped with a mechanical stirrer. The reactor was purged with argon and ethylene at 40 °C, and the ethylene pressure was kept at 1 bar. Then, the required amounts of hexane and 1-octene was added, and the reactor was saturated with ethylene for 1 h and heated to 60 °C. The hexane suspension of supported catalysts (PySTiTB or PySTiMAO) with TIBA or MMAO was prepared, and then injected into the reactor. The reactor was immediately pressurized to 5 bar and kept constant throughout the polymerization time. Termination was performed by venting the reactor, adding 1 ml methanol, and the polymerization product mixture was then precipitated in acidified methanol. The obtained copolymer was filtered and washed with methanol several times, followed by drying at 70 °C in air to a constant weight.

2.7. Analysis

High-resolution-inductively coupled plasma-mass-spectrometry (HR-ICP-MS) was run on an element 2 (Thermo Finnigan Bremen, Germany) by P. Klemens of this department. Infrared spectroscopy (IR) was run on a Mattson Galaxy 2030 FT-IR spectrometer by U. Zmij of this department. Elemental analysis was performed on a Heraeus Vario EL by W. Dindorf of this department. ²⁹Si CP-MAS solid-state NMR spectra (79.4 MHz) were recorded on a Bruker ASX-400 spectrometer operating at a field of 9.4 T. Molecular weights (*M_w*) and molecular weight distributions (*M_w/M_n*) of the resulting polymers were determined by high temperature GPC (PL-GPC210) at 135 °C using 1,2,4-trichlorobenzene as solvent by A. Jekel of the Center for Catalytic Olefin Polymerization at the Rijksuniversiteit Groningen, The Netherlands. The crystalline melting temperature (*T_m*) and crystallinity (*X_c*) of the polymers were determined by differential scanning calorimetry (DSC, NETZSCH DSC204) under nitrogen at 10 °C/min heating rate. The morphology of the supported catalysts and polymer products was examined on a DSM 962 scanning electron

microscope (SEM). The polymer bulk density was determined by weighing the polymer particles in the DSC aluminum pan of known volume. ^{13}C NMR spectra of copolymers were recorded at 135–145 °C on a Bruker DRX-400 spectrometer operating at 100.6 MHz. The copolymer sample was made up in 1,2,4-trichlorobenzene/deuterated *o*-dichlorobenzene (9:1, v/v) up to 10 wt.% in 5 mm NMR tube. The 1-octene content in the copolymer was determined according to the literature [32].

3. Results and discussion

3.1. Characterization of new supported titanium catalysts

The characterization of pyridylethylsilane-modified silica was performed by means of ^{29}Si CP-MAS

solid-state NMR and IR spectroscopy. In the ^{29}Si solid-state NMR spectrum (Fig. 1), the silicon signal of pyridylethylsilyl groups ($\equiv\text{Si}-\text{C}_2\text{H}_4-\text{C}_5\text{H}_4\text{N}$) grafted on silica surface was observed as a broad peak at -54 ppm and that of trimethylsilyl groups ($\equiv\text{Si}(\text{CH}_3)_3$), which were also introduced on the silica surface in order to reduce as many as possible the number of the remaining silanol groups ($\equiv\text{Si}-\text{OH}$), was observed in the most down field at -15 ppm. The signal of the remaining silanol groups of the calcined silica was, however, still observed as a small peak on the left shoulder of the very broad signal of internal silica's silicon in the most upper field. The graft of pyridylethylsilyl groups on silica was also confirmed by IR spectrum as shown in Fig. 2 (spectrum b). The small and broad absorption bands due to the C=N stretching of pyridine ring could be observed at about 1640 cm^{-1} , which is almost identical to that observed in poly(4-vinylpyridine) [33]. The strong absorption

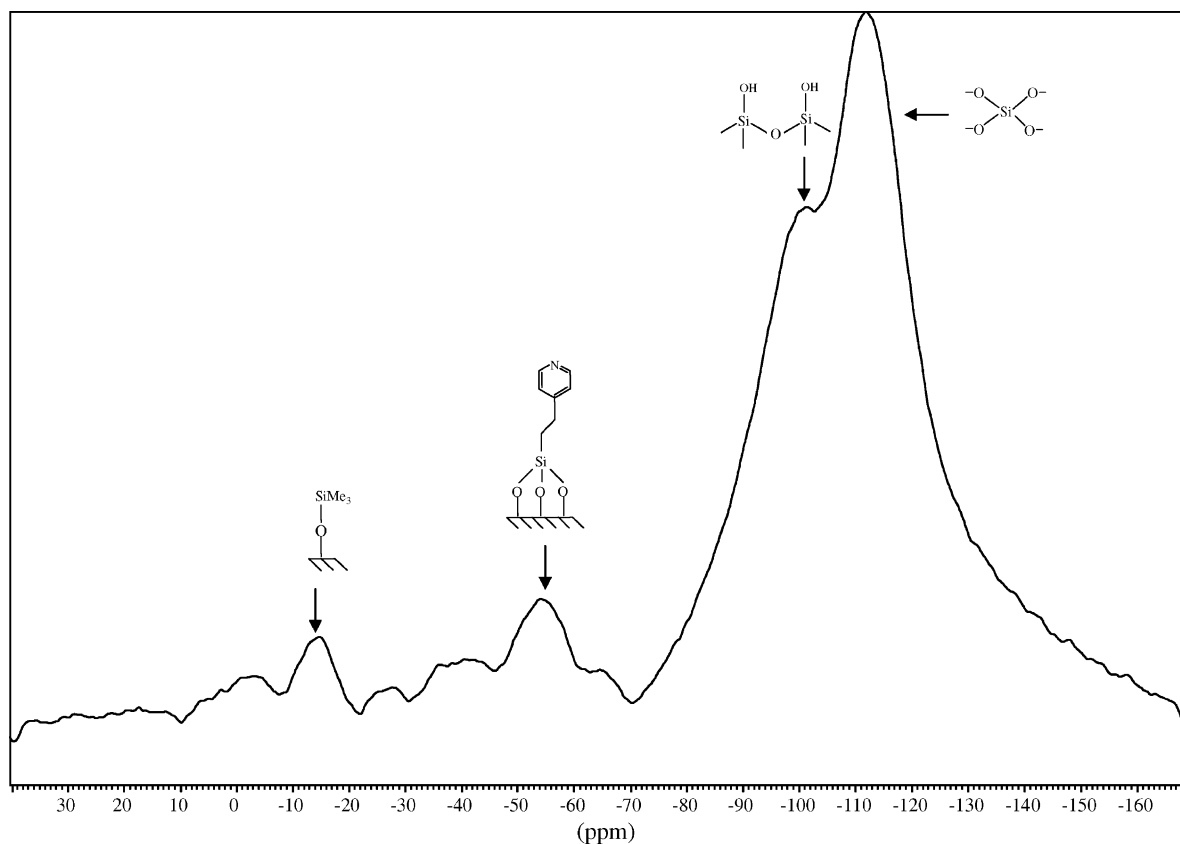


Fig. 1. ^{29}Si CP-MAS solid-state NMR spectrum of pyridylethylsilane-modified silica.

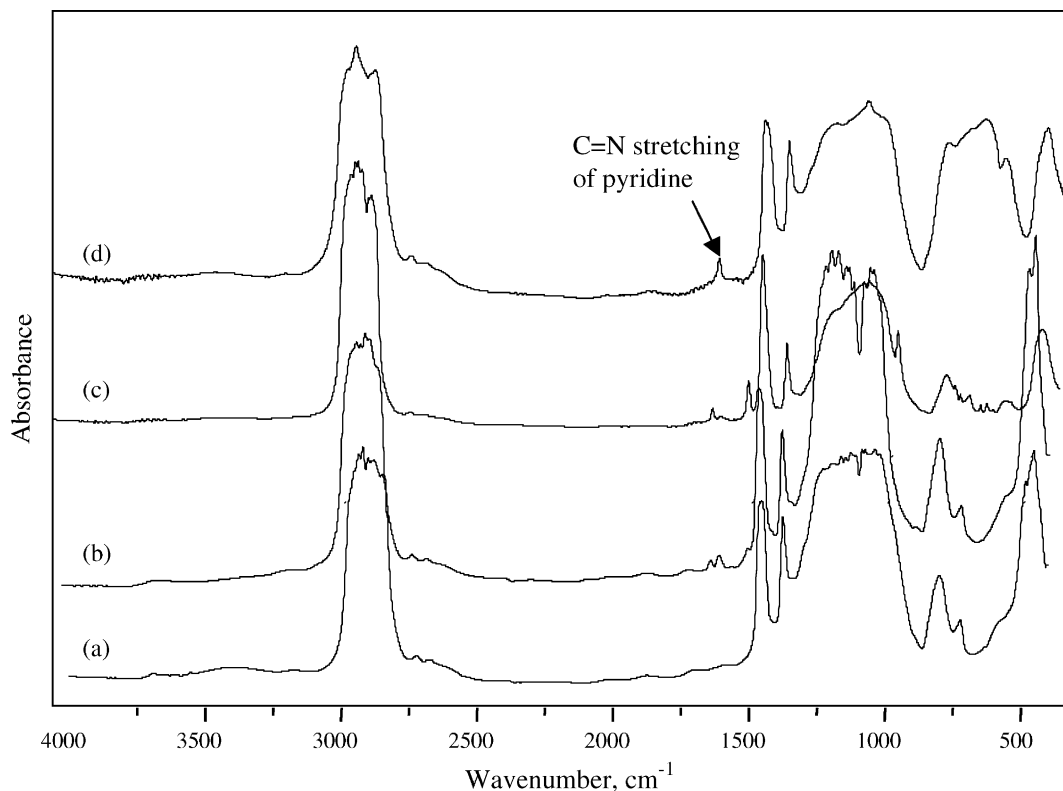


Fig. 2. IR spectra of lithiated silica (a), pyridylethylsilane-modified silica (b), PySTiTB (c) and PySTiMAO (d).

band observed between 2750 and 3000 cm^{-1} in all spectra could be assigned to the absorption due to the C–H stretching of the butyl groups grafted on the silica surface formed via the breaking of the siloxane bond, $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ during the lithiation process with *n*-BuLi to give $\equiv\text{Si}-\text{O}^-\text{Li}^+$ and $\equiv\text{Si}-\text{C}_2\text{H}_5$.

Both new supported CGCTiMe₂/TB (PySTiTB) and CGCTiCl₂/MAO (PySTiMAO) catalysts were characterized by IR, HR-ICP-MS and SEM. From the IR spectra in Fig. 2 (spectra c and d), we could observe that in both systems C=N stretching absorption band of pyridine ring appeared to be single and remarkably sharper compared to that of pyridylethylsilane-modified silica in spectrum b. This indicates the coordination of the pyridine nitrogen atoms to the active cationic titanium centers in both catalysts. The determination of the titanium, boron and aluminum contents of the supported catalysts was done by HR-ICP-MS spectrometry. The Ti and

B contents of PySTiTB were found to be 0.186 and 0.244 mmol/g, respectively, from which the B/Ti ratio of 1.3 could be obtained. With regard to the starting B/Ti ratio of 1 in the preparation step, the cationic titanium catalysts were coordinatively bound on pyridylethylsilane-modified silica with slightly excess amount of borate counter anions, which were also possibly physisorbed on the silica surface during the supporting step. For the PySTiMAO catalyst, the Ti and Al contents were found to be 0.043 and 4.67 mmol/g, respectively, giving the Al/Ti of about 110. The much lower content of Ti in PySTiMAO compared to PySTiTB might be possibly explained from the fact that the very bulky MAO molecules could block the coordination of the active titanium centers to the pyridine rings grafted on silica surface, and the excess of MAO used during the supporting step itself could also competitively coordinate to the pyridine rings or rapidly react with the remaining

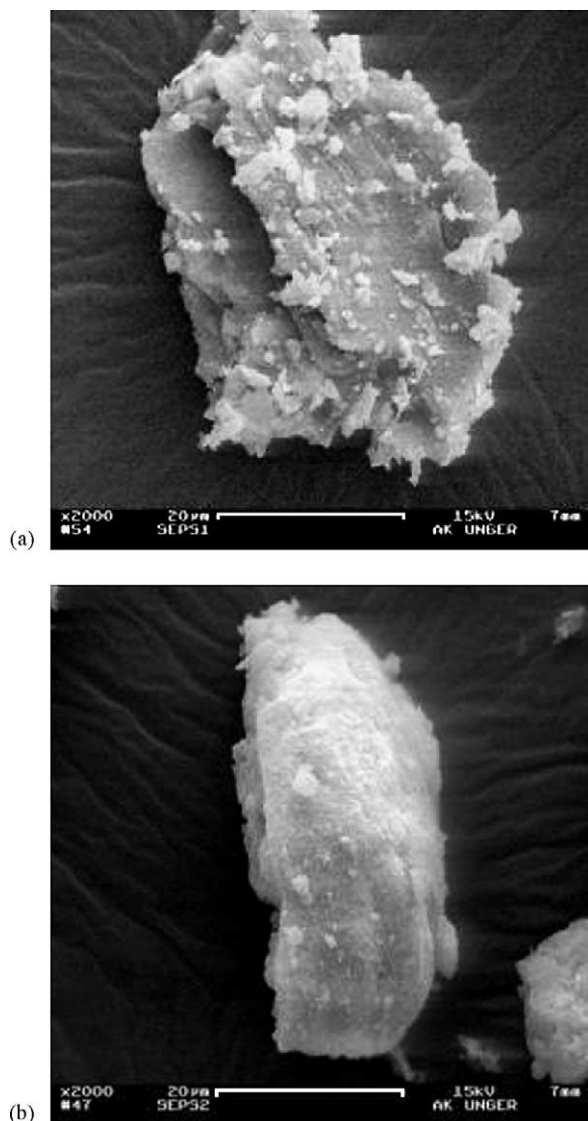


Fig. 3. SEM images of PySTiTB (a) and PySTiMAO (b).

silanol groups on the silica surface. From SEM images of the present supported catalysts (Fig. 3), we could observe the difference between the surfaces of PySTiTB and PySTiMAO. The homogeneous layer of MAO with active titanium catalysts inside could be seen in PySTiMAO, whereas the rough surface with small particles or perhaps the crystals of cationic titanium complexes was observed in PySTiTB.

3.2. Ethylene polymerization

The results of ethylene polymerization with PyS-TiTB in the presence of alkylaluminum compounds are summarized in Table 1. When no alkylaluminum was employed, no polymerization activity was observed, indicating sensitivity of this supported catalyst to impurities in the system. In the presence of TIBA, PySTiTB polymerized ethylene with relatively high activity, and the highest activity was achieved at Al/Ti of 280 at 162 kg PE/mol Ti·h (run 3), slightly higher than that observed in the corresponding homogeneous system (run 9). Above this ratio, the decrease of activity was observed, which might be due to the formation of the binuclear complexes of titanium and aluminum, as previously observed in the cationic zirconocene-catalyzed polymerization [34,35]. When the catalyst and TIBA were aged for 15 min, the activity slightly increased and reached 199 kg PE/mol Ti·h (run 6). Other alkylaluminum compounds like TEA and TMA were found to be inefficient for this system. This new supported cationic titanium catalyst could be considered as the new efficient supported catalyst for ethylene polymerization, having advantages over the conventional silica-supported cationic group 4 metal catalyst systems prepared by the pretreatment of the silica with alkylaluminum compounds to prevent the poisoning from silanol groups [25,26].

In Table 2, the results of ethylene polymerization with PySTiMAO in the presence of TIBA and MMAO as external aluminum compounds are summarized. It was found that PySTiMAO showed, in general, higher activity than PySTiTB. Interestingly, this supported catalyst polymerized ethylene with relatively high activity even without any external aluminum compound (run 1). However, the activity markedly increased when TIBA or MMAO were employed as external aluminum compounds. In the presence of common alkylaluminum like TIBA, the highest activity was achieved at 329 kg PE/mol Ti·h at Al/Ti = 560 (run 3), and the decrease of activity with higher Al/Ti ratio was also observed as in the case of PySTiTB. The aging of the catalyst was found to result in the decrease of activity by almost one-third (run 5), which is in contrast to what observed in PySTiTB system. When MMAO was employed as external aluminum compound instead of TIBA, the Al/Ti ratio of at least 2400 (run 6) was required in order to reach

Table 1

Ethylene polymerization with PySTiTB catalyst in the presence of alkylaluminums (AlR₃)^a

Run no.	AlR ₃	Al/Ti	Yield (g)	Activity (kg PE/mol Ti·h)	M _w (×10 ⁻³)	M _w /M _n	T _m ^b (°C)	X _c ^c (%)	Bulk density (g/cm ³)
1	No	0	0	–	–	–	–	–	–
2	TIBA	140	0.512	138	1136	1.8	134.6	54.3	0.32
3	TIBA	280	0.598	162	1056	2.6	135.4	54.5	0.33
4	TIBA	560	0.350	95	790	2.1	132.4	52.3	0.32
5 ^d	TIBA	280	0.123	33	1167	1.9	133.2	43.4	0.24
6 ^e	TIBA	280	0.697	199	1054	3.0	135.8	56.6	0.34
7	TEA	280	Trace	Trace	n.d. ^f	n.d.	n.d.	n.d.	n.d.
8	TMA	280	Trace	Trace	n.d.	n.d.	n.d.	n.d.	n.d.
9 ^g	TIBA	280	0.578	156	104	3.4	137.3	70.8	0.24

^a Polymerization conditions: in 100 ml Büchi glass reactor, solvent = hexane, total volume = 30 ml, ethylene pressure = 5 bar, polymerization temperature = 60 °C, polymerization time = 30 min, catalyst = 40 mg (Ti = 7.4 μmol).

^b Crystalline melting temperature.

^c Crystallinity determined from $X_c(\%) = (\Delta H_m / \Delta H_m^*) \times 100$, $\Delta H_m^* = 293$ J/g for HDPE.

^d Polymerization temperature = 25 °C.

^e Catalyst was aged at 25 °C for 15 min.

^f Not determined.

^g Homogeneous CGCTiMe₂/Ph₃C⁺B(C₆F₅)₄⁻ catalyst system: 30 ml hexane, ethylene pressure = 5 bar, polymerization temperature = 60 °C, polymerization time = 30 min, catalyst aging time (at 25 °C) = 15 min, Ti = 7.4 μmol, B/Ti = 2.

comparable activity, 240 kg PE/mol Ti·h, with that of PySTiMAO/TIBA system, and the increase of activity was observed with increasing Al/Ti ratio. The activity at Al/Ti = 2400 was found to be slightly lower than

that obtained with the corresponding homogeneous system (run 11).

To compare the catalytic behavior of PySTiTB and PySTiMAO in ethylene polymerization in the

Table 2

Ethylene polymerization with PySTiMAO catalyst in the presence of TIBA and MMAO as external aluminum compounds^a

Run no.	External Al compound	Al _{tot} /Ti	Yield (g)	Activity (kg PE/mol Ti·h)	M _w (×10 ⁻³)	M _w /M _n	T _m ^b (°C)	X _c ^c (%)	Bulk density (g/cm ³)
1	No	0	0.197	232	1205	3.0	135.2	43.7	0.30
2	TIBA	280	0.213	251	879	2.6	134.8	47.2	0.31
3	TIBA	560	0.280	329	584	3.4	135.3	52.0	0.30
4	TIBA	1200	0.051	60	571	2.5	134.2	21.5	0.29
5 ^d	TIBA	560	0.103	121	799	2.5	134.7	41.8	0.32
6	MMAO ^e	2400	0.204	240	429	8.6	136.0	59.3	0.32
7	MMAO	3600	0.445	524	303	7.5	139.1	69.7	0.28
8	MMAO	4800	0.710	835	317	13.4	138.8	69.5	0.22
9	MMAO	10000	1.412	1661	150	5.0	141.0	65.1	0.20
10 ^f	MMAO	560	Trace	Trace	n.d. ^g	n.d.	n.d.	n.d.	n.d.
11 ^f	MMAO	2400	0.321	378	47	3.6	133.4	81.6	0.10

^a Polymerization conditions: in 100 ml Büchi glass reactor, solvent = hexane, total volume = 30 ml, ethylene pressure = 5 bar, polymerization temperature = 60 °C, polymerization time = 30 min, catalyst = 40 mg (Ti = 1.7 μmol, Al/Ti = 110).

^b Crystalline melting temperature.

^c Crystallinity determined from $X_c(\%) = (\Delta H_m / \Delta H_m^*) \times 100$, $\Delta H_m^* = 293$ J/g for HDPE.

^d Catalyst was aged at 25 °C for 15 min.

^e 10 wt.% TIBA-containing MAO in heptane solution.

^f Homogeneous CGCTiCl₂/MMAO catalyst system: 30 ml hexane, ethylene pressure = 5 bar, polymerization temperature = 60 °C, polymerization time = 30 min, catalyst aging time (at 25 °C) = 15 min, Ti = 1.7 μmol.

^g Not determined.

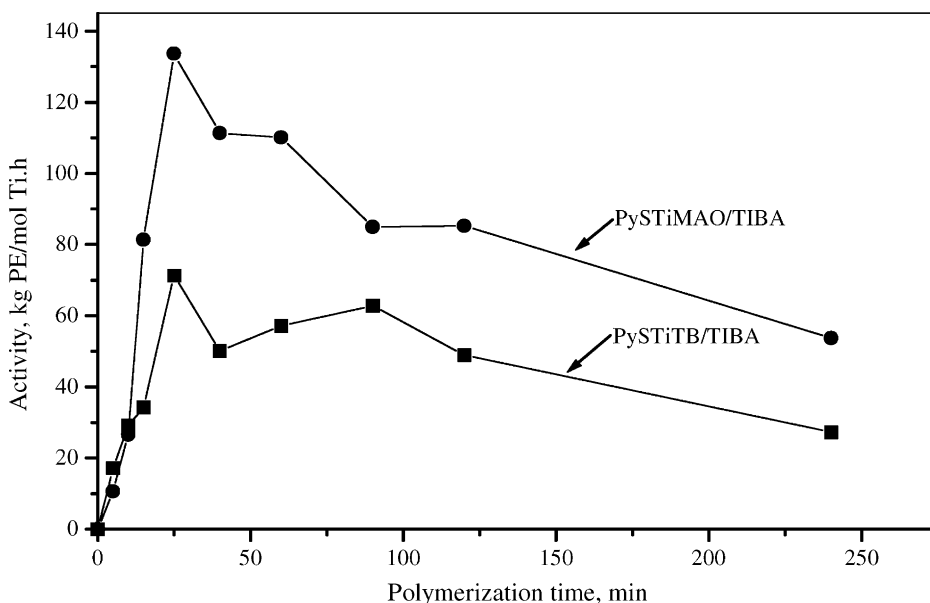


Fig. 4. Activity–time profiles of the representative 4 h ethylene polymerization for PySTiTB/TIBA and PySTiMAO/TIBA.

presence of TIBA, the activity–time profile of the representative 4 h ethylene polymerization was investigated, as shown in Fig. 4. The activity profiles of both supported catalysts were the same at the initial polymerization time shorter than 15 min. PySTiMAO showed, however, after 15 min almost double activity of that of PySTiTB. The profiles of both systems reached the highest activities at 30 min polymerization time. Then, the gradual decrease of activity throughout the polymerization time of 4 h was observed in PySTiMAO system. In contrast, the activity profile of PySTiTB was found to decrease after 30 min, and then started to increase again up to the turning point at 90 min polymerization time before the gradual decrease. The different catalytic behavior observed in these two supported catalysts might indicate that the fragmentation of PySTiTB due to the growing polymer chains within the pores to give more accessible active sites is responsible for the increase of the activity between 40 and 90 min polymerization time. The gradual decrease of the activity observed in PySTiMAO is perhaps due to the difficulty of the diffusion of ethylene through the outer polymer layer with increasing polymerization time. According to the reports on ethylene and propylene polymerization with silica-supported zirconocene/MAO by Fink and

co-workers [22,36], it could, therefore, imply that the active sites were formed mainly within the pores of silica in the case of PySTiTB system, but mainly on the outer surface of silica in the case of PySTiMAO system.

3.3. Properties of the resulting polyethylenes

As shown in Table 1, the molecular weights (M_w) of polyethylenes obtained with PySTiTB/TIBA catalyst system are remarkably high in the range of 10^6 , which are 10 times higher than that of polymer obtained with the corresponding homogeneous system. The molecular weights were also found to decrease with increasing Al/Ti ratio, indicating possible termination via chain transfer to aluminum. The molecular weight distributions (MWDs) are narrow and in the range of normal single-site catalyst ($M_w/M_n = 1.8\text{--}3.0$). The crystalline melting temperatures (T_m) and crystallinities (X_c) are in the range of high density polyethylene (HDPE), but slightly lower than that of polyethylene obtained with the homogeneous system. The average bulk density is 0.33 g/cm^3 , higher than that of polyethylene obtained with the homogeneous system. From SEM image as shown in Fig. 5a, the polyethylene obtained with PySTiTB/TIBA system

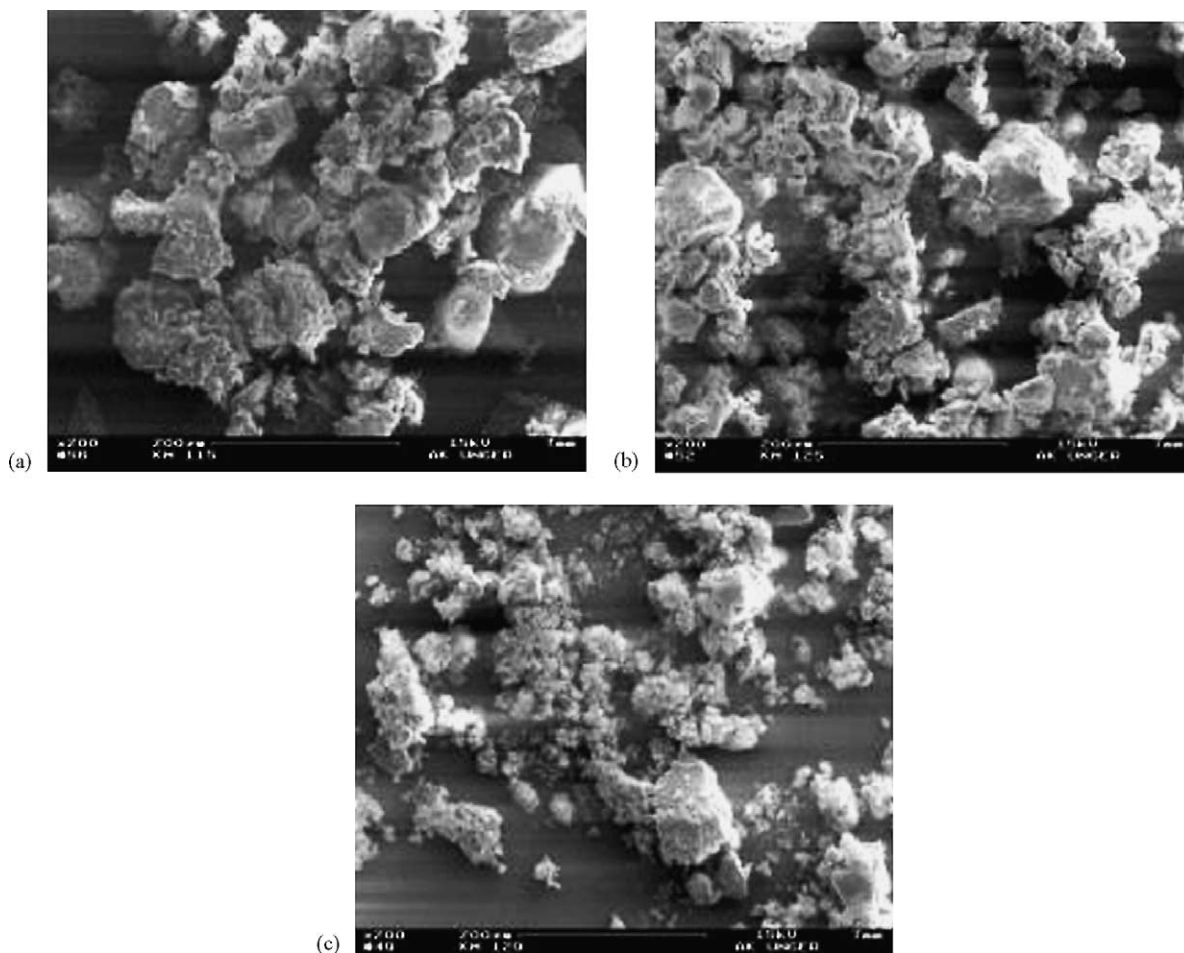


Fig. 5. SEM images of polyethylenes obtained with PySTiTB/TIBA from run 3 in Table 1 (a), PySTiMAO/TIBA from run 3 in Table 2 (b) and PySTiMAO/MMAO from run 8 in Table 2 (c).

was found to replicate the shape of the supported catalyst.

From Table 2, the molecular weights of polyethylenes obtained with PySTiMAO system were found to vary from 1.5×10^5 up to as high as 1.2×10^6 . PyS-TiMAO/TIBA system produced polyethylenes with much higher M_w than PySTiMAO/MMAO system. Surprisingly, the highest M_w of 1.2×10^6 , which is slightly higher than that of polyethylene produced by PySTiTB/TIBA system, was achieved by PyS-TiMAO without any external aluminum compound. The decrease of M_w with increasing Al/Ti ratio was observed both in TIBA and MMAO systems. MWDs of polyethylenes obtained with PySTiMAO/TIBA

system are in the range of normal single-site catalyst ($M_w/M_n = 2.5\text{--}3.4$), whereas PySTiMAO/MMAO system produced polyethylenes with very broad MWDs varying from 5 to 13.4. T_m and X_c of polyethylenes obtained with both PySTiMAO/TIBA and PySTiMAO/MMAO systems are in the range of HDPE, but higher T_m and X_c could be observed in the latter system. The bulk densities of polyethylenes obtained with PySTiMAO/TIBA system are in the range of $0.29\text{--}0.32\text{ g/cm}^3$, while those of polymers obtained with PySTiMAO/MMAO system are somewhat lower, and found to decrease with increasing Al/Ti ratio. The broad MWDs and low bulk densities observed in PySTiMAO/MMAO system are believed

to be the result from the leaching of some active titanium catalysts from the silica matrix due to breaking of the coordination interaction between pyridine rings and cationic titanium centers by MMAO, leading to final polymer mixtures of polyethylenes produced on the silica support and in the homogeneous phase. The SEM image of polyethylene produced with PySTiMAO/MMAO system in Fig. 5c showed fine polymer particles, supporting this phenomenon.

3.4. Ethylene copolymerization with 1-octene

The results of ethylene copolymerization with 1-octene are summarized in Table 3. The copolymerization was carried out with 1-octene concentration in feed at 0.08, 0.2 and 0.4 M, and the Al/Ti ratios used for PySTiTB/TIBA, PySTiMAO/TIBA and PySTiMAO/MMAO systems are 280, 560 and 3600, respectively. Overall, the activities of these three supported catalyst systems in ethylene copolymerization with 1-octene were found to be much lower than those observed for each system in ethylene homopolymerization (see Tables 1 and 2). By comparing the results at the same 1-octene concentration in feed, PySTiMAO/TIBA was found to show the lowest activity. The activity profiles versus 1-octene in feed, as shown in Fig. 6, of PySTiTB/TIBA and PySTiMAO/TIBA

systems showed the so-called comonomer effect, when 1-octene concentration was increased from 0.08 to 0.2 M, i.e. the activity in ethylene polymerization increased in the presence of a small amount of α -olefin as comonomer [37,38]. The activities were, however, observed to decrease at 1-octene concentration of 0.4 M. This might be due to the blocking of the active sites by 1-octene at high concentration. On the other hand, this behavior was not observed for the PySTiMAO/MMAO system, where the activity was found to be almost unchanged with increasing 1-octene concentration. The activities observed with the corresponding homogeneous systems (runs 13 and 14) were found to be remarkably higher than those of the supported systems.

3.5. Properties of the resulting copolymers

The 1-octene contents in the resulting copolymers obtained with PySTiTB/TIBA are the lowest when compared among the three supported catalyst systems. PySTiMAO/MMAO was found to be the most efficient system to achieve higher incorporation of 1-octene in the copolymer. The presented supported catalysts, however, produced copolymers with much lower 1-octene contents than the corresponding homogeneous systems. The example of ^{13}C NMR spectrum

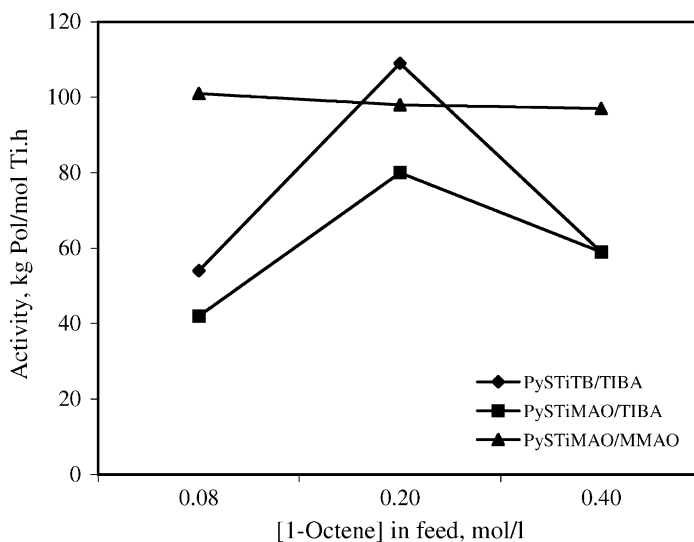


Fig. 6. Effect of 1-octene concentration in feed on copolymerization activity.

Table 3
Ethylene/1-octene copolymerization with PySTiTB (I) and PySTiMAO (II) catalysts in the presence of TIBA and MMAO as external aluminum compounds^a

Run no.	Catalyst	External Al compound	Al _{tot} /Ti	1-Octene in feed (mol/l)	Yield (g)	Activity (kg Pol/mol Ti·h)	M_w ($\times 10^{-3}$)	M_w/M_n	1-Octene content ^b (mol%)	T_m^c (°C)	X_c^d (%)
1	I	TIBA	280	0.08	0.297	54	1198	2.3	0.5	128.7	51.4
2	I	TIBA	280	0.20	0.607	109	957	2.6	1.6	125.7	44.3
3	I	TIBA	280	0.40	0.327	59	832	3.5	2.3	124.8	41.4
4	II	TIBA	560	0.08	0.053	42	n.d. ^c	n.d.	n.d.	121.4	48.5
5	II	TIBA	560	0.20	0.102	80	n.d.	n.d.	n.d.	122.5	40.3
6 ^f	II	TIBA	560	0.20	0.294	115	512	3.9	6.2	122.5	24.2
7	II	TIBA	560	0.40	0.076	59	n.d.	n.d.	n.d.	121.3	38.7
8	II	MMAO	3600	0.08	0.129	101	286	15.0	2.5	123.8	40.4
9	II	MMAO	3600	0.20	0.125	98	293	25.0	6.4	124.8	28.1
10 ^f	II	MMAO	3600	0.20	1.165	457	55	3.0	15.4	71.6/122.9	10.0
11	II	MMAO	3600	0.40	0.124	97	546	3.5	8.4	123.8	15.3
12 ^g	CGCTiMe ₂ /TB/TIBA	–	280	0.20	0.185	33	n.d.	n.d.	n.d.	61.7/123.0	7.4
13 ^h	CGCTiMe ₂ /TB/TIBA	–	280	0.20	4.290	728	120	1.4	11.7	94.0	19.1
14 ⁱ	CGCTiCl ₂ /MMAO	–	3600	0.20	1.114	437	18	1.7	14.2	74.2/122.3	11.1

^a Polymerization conditions: in 200 ml Büchi glass reactor, solvent = hexane, total volume = 80 ml, ethylene pressure = 5 bar, polymerization temperature = 60 °C, polymerization time = 45 min, catalyst = 40 mg (Ti = 7.4 μ mol for PySTiTB and Ti = 1.7 μ mol, Al/Ti = 110 for PySTiMAO).

^b Determined by ¹³C NMR.

^c Crystalline melting temperature.

^d Crystallinity determined from $X_c(\%) = (\Delta H_m / \Delta H_m^*) \times 100$, $\Delta H_m^* = 293$ J/g for HDPE.

^e Not determined.

^f Ti = 3.4 μ mol.

^g Homogeneous system in hexane: Ti = 3.4 μ mol, B/Ti = 2.

^h Homogeneous system in toluene.

ⁱ Homogeneous system in hexane: Ti = 3.4 μ mol.

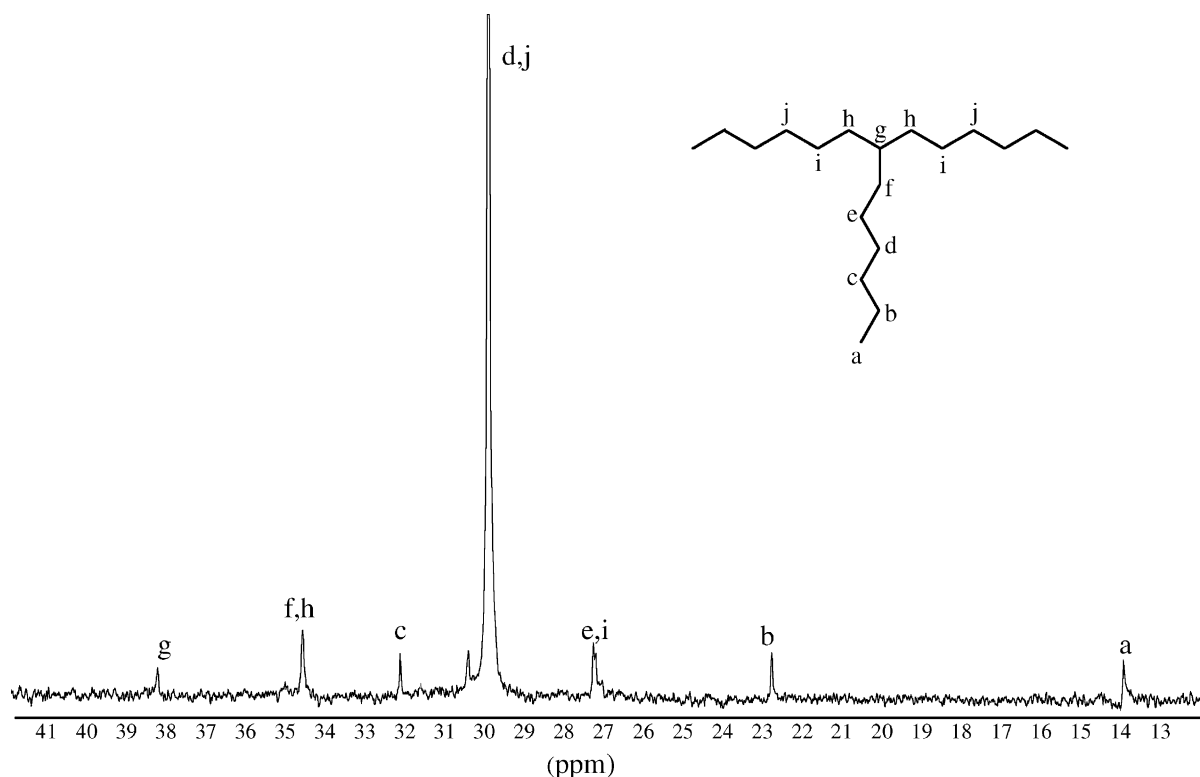


Fig. 7. ^{13}C NMR spectrum of ethylene/1-octene copolymer obtained with PySTiMAO/TIBA (run 6 in Table 3).

of the resulting copolymer is shown in Fig. 7. PySTiTB/TIBA gave the copolymers with markedly high M_w , the highest value of about 1.2×10^6 at 0.08 M 1-octene concentration. M_w was also found to decrease with increasing 1-octene concentration, indicating the possible chain transfer to comonomer in termination step. The MWDs are in the normal range for single-site catalysts. In contrast, the copolymers obtained with PySTiMAO/TIBA and PySTiMAO/MMAO systems show much lower M_w , and MWDs were found as bimodal and in the wide range varying from 3.0 up to as broad as 25. From the GPC curves in Fig. 8, we could observe two fractions of the copolymer sample from run 9 in Table 3 ($MWD = 25$), the low molecular weight fraction observed at the elution time close to that of the copolymer obtained with homogeneous system (run 14 in Table 3) and the high molecular weight fraction observed as broad curve at the faster elution time in homopolyethylene area, as compared with the curve

of PE from run 8 in Table 2. When the amounts of Ti and MMAO were doubled (run 10 in Table 3), only the curve at the low molecular weight area, which is almost identical to that of the homogeneous system, was observed. Thus, it could be concluded that this low molecular weight fraction is the low molecular weight ethylene/1-octene copolymer produced in the homogeneous phase. The possibility of leaching increases with the increasing amount of MMAO in the system, as seen in run 10 Table 3, and the homopolymerization results in Table 2. The unusually broad curve in the homopolyethylene area might be due to the presence of two or more active species, which is perhaps associated with the chemical heterogeneity formed by MMAO, on the silica surface. The same bimodal and broad MWDs are also observed in ethylene/1-hexene copolymers produced with silica-supported *rac*- $\text{Me}_2\text{Si}[2\text{-Me-4-Ph-Ind}]_2\text{ZrCl}_2/\text{MAO}$ in the presence of TIBA as reported by Fink and co-workers [21]. T_m and X_c of the resulting copolymers

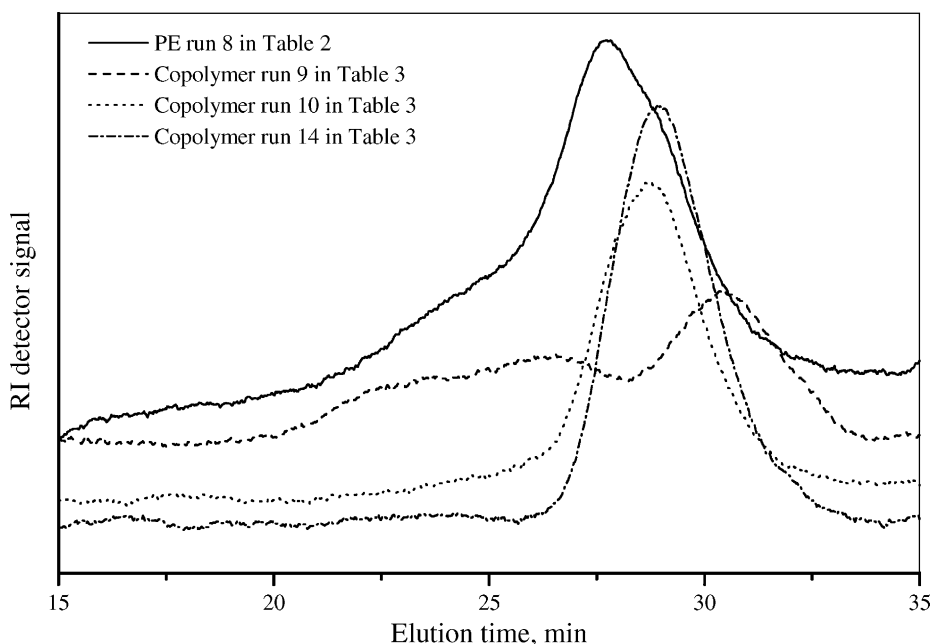


Fig. 8. GPC curves of polyethylene and ethylene/1-octene copolymers obtained with PySTiMAO/MMAO.

are, in overall, in the range of 121–129 °C and 10–52%, respectively. The decrease of T_m and X_c with increasing 1-octene concentration and 1-octene content in copolymer was clearly observed in PySTiTB/TIBA system. On the other hand, the change of T_m of the copolymers obtained with PySTiMAO/TIBA and PySTiMAO/MMAO are not clearly correlated to the 1-octene concentration, but only the decrease of X_c was observed to be more strongly dependent on the 1-octene concentration than that observed in PySTiTB/TIBA system.

4. Conclusions

Two new supported-type linked cyclopentadienyl-amido titanium catalysts, PySTiTB and PySTiMAO, were prepared by immobilizing $Ti(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\text{Me}_2/\text{Ph}_3\text{C}^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ and $Ti(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}^t\text{Bu})\text{Cl}_2/\text{MAO}$ on pyridylethylsilane-modified silica. These supported titanium catalysts showed relatively high activities in ethylene polymerization and modest activities in ethylene copolymerization with 1-octene in the presence of TIBA or MMAO. PySTiTB gave polyethylenes with M_w

slightly above 10^6 and narrow MWDs, while PySTiMAO produced polyethylene with M_w ranging from 1.5×10^5 to 1.2×10^6 and narrow MWDs when combined with TIBA, but very broad MWDs ($M_w/M_n = 5.0\text{--}13.4$) when MMAO was used. All the polyethylene products were obtained as free-flowing particles with relatively high bulk densities. Ethylene/1-octene copolymers obtained with both supported catalysts have lower 1-octene contents compared to those obtained with the corresponding homogeneous systems. PySTiMAO when combined with MMAO gave the copolymers with highest 1-octene contents, but the MWDs of the resulting copolymers were found to be in a wide range varying from 3.0 up to as broad as 25. The markedly broad MWDs of the homopolymers and copolymers obtained with PySTiMAO/MMAO system are considered to be the result from the leaching of titanium catalysts, as confirmed by SEM images and GPC results.

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References

- [1] J.C.W. Chien, D. He, *J. Polym. Sci., Polym. Chem.* 29 (1991) 1603.
- [2] K. Soga, M. Kaminaga, *Makromol. Chem.* 194 (1993) 1745.
- [3] W. Kaminsky, *Macromol. Symp.* 97 (1995) 79.
- [4] H.C. Welborn, US Patent 4808561 (1989); *Chem. Abstr.* 106 (1987) 157033.
- [5] M.F.H. Van Tol, J.A.M. van Beek, *PCT Int. Appl.* 97/42228 (1997); *Chem. Abstr.* 128 (1998) 23277.
- [6] D.G. Ward, E.M. Carnahan, *PCT Int. Appl.* 96/23005 (1996); *Chem. Abstr.* 125 (1996) 196699.
- [7] J. Tian, S. Wang, Y. Feng, J. Li, S. Collins, *J. Mol. Catal. A: Chem.* 144 (1999) 137.
- [8] S.J. Lancaster, S.M. O'Hara, M. Bochmann, in: W. Kaminsky (Ed.), *Metalorganic Catalysts for Synthesis and Polymerization*, Springer, Berlin, 1999, p. 413.
- [9] N. Kishi, C.-H. Ahn, J. Jin, T. Uozumi, T. Sano, K. Soga, *Polymer* 41 (2000) 4005.
- [10] S.B. Roscoe, J.M.J. Frechet, J.F. Walzer, A.J. Dias, *Science* 280 (1998) 270.
- [11] K. Musikabhumma, T.P. Spaniol, J. Okuda, *Macromol. Chem. Phys.* 203 (2002) 115.
- [12] K. Soga, M. Kaminaka, *Makromol. Chem. Rapid Commun.* 12 (1991) 367.
- [13] W. Kaminsky, F. Renner, *Makromol. Chem. Rapid Commun.* 14 (1993) 239.
- [14] K. Soga, T. Uozumi, M. Saito, T. Shiono, *Macromol. Chem. Phys.* 195 (1993) 1503.
- [15] K. Soga, H.J. Kim, *Makromol. Chem. Rapid Commun.* 15 (1994) 139.
- [16] K. Soga, in: K. Soga, M. Terano (Ed.), *Catalyst Design for Tailor-Made Polyolefins*, Koudansha-Elsevier, Tokyo, 1994, p. 307.
- [17] J.H.Z. dos Santos, A. Larentis, M.B. da Rosa, F.C. Stedile, J. Dupont, M.M.deC. Forte, I.J.R. Baumvol, *Macromol. Chem. Phys.* 198 (1997) 3529.
- [18] M.C. Sacchi, D. Zucchi, I. Tritto, P. Locatelli, *Macromol. Rapid Commun.* 16 (1995) 581.
- [19] J.C.W. Chien, B.-P. Wang, *J. Polym. Sci., Part A: Polym. Chem.* 26 (1988) 3089.
- [20] J.C.W. Chien, B.-P. Wang, *J. Polym. Sci., Part A: Polym. Chem.* 28 (1990) 15.
- [21] C. Przybyla, B. Tesche, G. Fink, *Macromol. Rapid. Commun.* 20 (1999) 328.
- [22] G. Fink, B. Steinmetz, B. Tesche, *Chem. Rev.* 100 (2000) 1377.
- [23] M. Koch, M. Stork, M. Klapper, K. Müllen, H. Gregorius, *Macromolecules* 33 (2000) 7713.
- [24] M. Koch, A. Falcou, N. Nenov, M. Klapper, K. Müllen, *Macromol. Rapid. Commun.* 22 (2001) 1455.
- [25] G.G. Hlatky, D.J. Upton, H.W. Turner, *PCT Int. Appl.* 91/09982 (1991); *Chem. Abstr.* 115 (1991) 242266.
- [26] G.G. Hlatky, D.J. Upton, *Macromolecules* 24 (1996) 8019.
- [27] K. Musikabhumma, T. Uozumi, T. Sano, K. Soga, *Macromol. Rapid Commun.* 21 (2000) 675.
- [28] F. Amor, J. Okuda, *J. Organomet. Chem.* 520 (1996) 245.
- [29] J. Okuda, T. Eberle, T.P. Spaniol, *Chem. Ber.* 130 (1997) 209.
- [30] P.-J. Sinnema, Ph.D. Thesis, Rijksuniversiteit Groningen, The Netherlands, 1999.
- [31] C. du Fresne von Hohenesche, Diploma Thesis, Mainz University, Germany, 1999.
- [32] K. Kimura, S. Yuasa, Y. Maru, *Polymer* 25 (1984) 441.
- [33] T. Balakrishnan, V. Rajendran, *J. Polym. Sci., Part A: Polym. Chem.* 35 (1997) 727.
- [34] M. Bochmann, S.J. Lancaster, *Angew. Chem., Int. Ed. Engl.* 33 (1994) 1634.
- [35] M. Bochmann, S.J. Lancaster, *J. Organomet. Chem.* 497 (1995) 55.
- [36] R. Goretzki, G. Fink, B. Tesche, B. Steinmetz, R. Rieger, W. Uzick, *J. Polym. Sci., Part A: Polym. Chem.* 37 (1999) 677.
- [37] N. Herfert, P. Montag, G. Fink, *Makromol. Chem.* 194 (1993) 3167.
- [38] R. Kravchenko, R.M. Waymouth, *Macromolecules* 31 (1998) 1.