

Vanadium Complex with Tetradentate [O,N,N,O] Ligand Supported on Magnesium Type Carrier for Ethylene Homopolymerization and Copolymerization

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ABSTRACT: Immobilization of 1,2-cyclohexylenebis(5-chlorosalicylideneiminato)vanadium dichloride on the magnesium support obtained in the reaction of $\text{MgCl}_2 \cdot 3.4\text{EtOH}$ with Et_2AlCl gives a highly active precursor for ethylene homopolymerization and its copolymerization with 1-octene. This catalyst exhibits the highest activity in conjunction with MAO, but it is also highly active with AlMe_3 as a cocatalyst. On the other hand, when combined with chlorinated alkylaluminum compounds, Et_2AlCl and EtAlCl_2 , it gives traces of polyethylene. Moreover, its catalytic activity is strongly affected by the reaction temperature: it increased with rising polymerization temperature from 20 °C

to 60 °C. The kinetic curves obtained for the supported vanadium catalyst, in contrast to its titanium analogue, are of decay type, yet the reduction in the polymerization rate is rather moderate in the early stages of polymerization, and then it is relatively very slow. The vanadium catalyst gives copolymers at a lower yield than the titanium one does, but with the significantly higher 1-octene content. © 2009 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 48: 471–478, 2010

KEYWORDS: copolymerization; polyethylene; supports; vanadium complex; Ziegler-Natta polymerization

INTRODUCTION Vanadium-based Ziegler-Natta catalysts are well known for their ability to produce such polymers as high molecular weight polyethylene, ethylene/1-olefin copolymers with a high 1-olefin content, syndiotactic propylene; they are able to polymerize olefins in the living manner, and they are employed in the synthesis of poly(ethylene-co-propylene) and poly(ethylene-co-propylene-co-diene) elastomers.^{1,2} Despite that fact, vanadium catalysts have for many years attracted much less interest than the catalytic systems which were based on Group 4 metals (predominantly Ti and Zr). Only recently, vanadium complexes bearing various supporting ligands such as *N,N,N*-tridentate (pyrazolyl-pyridine),³ arylimido-aryloxo,⁴ salicylaldiminato,⁵ O,N,N,O-type amine bis(phenolate),⁶ β -enaminoketonato,⁷ amide⁸ and others⁹ have been reported as effective catalysts for olefin homopolymerization and copolymerization. As part of ongoing study in this area, we have recently used O,N,N,O-tetradentate salen type ligands on vanadium complexes.¹⁰ However, the presence of the supporting ancillary ligands in those novel vanadium catalysts did not eliminate the disadvantages of classical Ziegler-Natta vanadium-based catalysts, such as decay of activity during polymerization and low thermal stability. Low stability of vanadium catalysts during polymerization is mainly attributed to susceptibility of vanadium species to reduction during the catalytic cycle to the

inactive divalent state.^{1(a)} One of the ways to overcome these problems is immobilization of vanadium catalysts on inorganic carriers.¹¹ Indeed, immobilization of ethylenebis(5-chlorosalicylideneiminato)vanadium dichloride on $\text{MgCl}_2(\text{THF})_2$ modified by Et_2AlCl give the catalyst which is resistant to deactivation within the temperature range studied (30–60 °C) and which offers a long lifetime.¹² In this article, we report the results of ethylene homopolymerization and copolymerization performed in the presence of 1,2-cyclohexylenebis(5-chlorosalicylideneiminato)vanadium dichloride immobilized on another magnesium type carrier, namely on the carrier obtained in the reaction of $\text{MgCl}_2 \cdot 3.4\text{EtOH}$ and Et_2AlCl .

EXPERIMENTAL

General Methods

All manipulations were performed under argon or nitrogen atmosphere, with the use of the standard Schlenk and glove box techniques. Powder X-ray diffraction (XRD) patterns of magnesium supports were obtained with the use of the HZG-4 instrument with $\text{Cu K}\alpha_1$ radiations. The samples were covered with a PE film to avoid any contact with air. The infrared spectra of supports and supported precatalysts were recorded on the Nicole Nexus 2002 FTIR spectrometer. Samples were prepared under the inert atmosphere in nujol.

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Scanning electron micrographs were obtained with the use of Philips XL 30 ESEM/TMP. Molecular weight and molecular weight distribution ($\overline{M}_w/\overline{M}_n$) data for the resulting polymers were determined by means of gel permeation chromatography (Alliance 135 GPCV 2000 apparatus from Waters) at 135 °C. Trichlorobenzene was applied as a solvent, and its flow rate was set up at 0.6 mL/min. Narrow molecular weight distribution polystyrene standards were used for calibration. Differential scanning calorimetry (DSC) analyses were carried out with the 2010 DSC calorimeter (TA Instruments). The polymer samples were first heated up to 170 °C at the rate of 10 K/min to remove thermal history, and then they were cooled down. The second heating cycle was used for collecting DSC thermogram data. The number of branches in polyethylene and copolymer composition (according to ref. 13) were determined by FTIR using the Nicole Nexus 2002 FTIR spectrometer. The samples were used in the form of polymer powder pills with KBr. The particle size distribution was analyzed with the use of the vibratory sieve shaker from Fritsch. Every polymer sample was shaken over 20 min using the set of sieves with the mesh size within 2.0–0.063 mm.

Materials

Ethylene (3.0 grade, Linde Gas) was purified by passing it over a column of sodium metal supported on Al_2O_3 . Solvents were distilled from sodium (toluene) or sodium/benzophenone (hexane). 1-Octene was dried over 4 Å and 13X molecular sieves. MAO (Witco, 10.0 wt %), Et_2AlCl (Aldrich, 1 M), EtAlCl_2 (Aldrich, 1.8 M), Et_3Al (Aldrich, 1.9 M), Me_3Al (Witco, 2 M) were used as received. The vanadium complex (1,2-cyclohexylenebis(5-chlorosalicylideneiminato)vanadium dichloride) was prepared according to the procedure which is available in the reports,¹⁰ by the reaction of the ligand with VCl_4 in CH_2Cl_2 , at room temperature, overnight.

Preparation of the Support and the Supported Catalyst

The support preparation was performed by the addition of Et_2AlCl (38 mL, 1 M) to the suspension of $\text{MgCl}_2 \cdot 3.4\text{EtOH}$ (3.083 g) in hexane, at 0 °C. The reaction was initially run at low temperature, and then at room temperature for 1.5 h. The solid product was filtered off, washed with hexane, and dried under argon flow, and subsequently under vacuum. The amount of Al present in the support was 7.8 wt %. The detailed procedure was described in ref. 14. Immobilization of vanadium complexes was effected exactly in the same way as immobilization of titanium complexes with the same structures, which was presented in.¹⁴ The vanadium complex was ball-milled with the magnesium support (1.1443 g) in hexane/toluene at room temperature for 20 h. The resulting solid was separated, washed several times with toluene and hexane and dried until free-flowing under argon, and then under vacuum.

Ethylene Homopolymerization and Copolymerization

The ethylene polymerization was performed in a Büchi autoclave. Hexane (0.15 L) was introduced to the reactor and then, as the set temperature was reached, the required amounts of cocatalyst and precatalyst were injected. After-

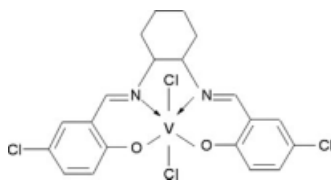
wards, the reactor was pressurized with ethylene and the pressure (5 atm) was kept constant throughout the run. At the end of polymerization, i.e., usually after 30 min, the ethylene pressure was released, acidified methanol was added and the polymer was separated from the reaction mixture by filtration. It was washed several times with methanol and dried *in vacuo*. Ethylene polymerization kinetics was measured with the use of a mass flowmeter. The ethylene/1-octene copolymerization process followed the procedure for ethylene homopolymerization; the only difference was that a higher 1-olefin was introduced to the reactor before the catalytic components were added there.

RESULTS AND DISCUSSION

The recent findings which revealed that immobilization of various types of nonmetallocene catalysts on magnesium supports obtained by the reaction of an alkylaluminum compound with a MgCl_2 /alcohol adduct yields highly active polymerization catalysts,¹⁵ often with stable polymerization activity^{15(a)}, made us employ that type of support for immobilization of 1,2-cyclohexylenebis(5-chlorosalicylideneiminato)titanium dichloride.¹⁴ In this study, we used the same support obtained in the reaction of $\text{MgCl}_2 \cdot 3.4\text{EtOH}$ and Et_2AlCl for immobilization of the vanadium complex having the identical tetradentate [O,N,N,O]-type ligand (Scheme 1). We aimed at two targets at the same time. First of all, we wanted to check how the catalytic properties of the salen-type vanadium complex change after its immobilization on the magnesium carrier, and the second goal was to compare the catalytic behavior of the supported titanium and vanadium complexes in order to gain a better insight into the effects of the type of the transition metal which is used in a catalyst on the catalytic performance of that catalyst.

Synthesis and Characterization of Supported Vanadium Catalyst

As we mentioned earlier, we used the adduct of magnesium chloride and ethyl alcohol, $\text{MgCl}_2 \cdot 3.4\text{EtOH}$, modified by Et_2AlCl , as a support. Alkylaluminum ethoxide is produced in that reaction, majority of which will be eluted from the solid product in the solvent wash operation, and the residual alkylaluminum ethoxide has the form of coordinatively bridged species: Mg-O(Et)-Al and, when Et_2AlCl is used, also the Cl bridge between Al and Mg is formed.¹⁶ To observe the changes in the support during its modification, the initial magnesium compound and the carrier materials obtained from its reaction with an organoaluminum compound were subjected to FTIR and XRD analysis. The XRD patterns are shown in Figure 1. Anhydrous MgCl_2 is known to have the structure which gives the strong XRD pattern at $2\theta = 35^\circ$, 15° , and 50° ,¹⁷ while we do not observe any pattern at $2\theta = 50^\circ$ for the adduct of MgCl_2 with EtOH, and a new peak at about $2\theta = 10^\circ$ appears. The diffraction pattern of the modified support is much simpler than that for the magnesium adduct but some similarities are clearly seen (for example the reflection at $2\theta = 15^\circ$ or 31°). Nevertheless, the broad diffraction peaks indicating a high degree of crystallographic disorder are not present. Thus, the used support show the



SCHEME 1 The structure of vanadium complex with tetradentate [O,N,N,O] ligand.

XRD pattern different from those obtained for supports prepared via reaction of AlEt_3 or $\text{Al}i\text{Bu}_3$ with $\text{MgCl}_2/\text{EtOH}$ adducts¹⁸ and this could indicate that reaction between AlEt_2Cl and the EtOH present in the adduct with MgCl_2 was not complete. The analysis of the FTIR spectra confirmed the reaction between an organoaluminum compound and ethanol in the carrier. As can be seen (Fig. 2), the absorption band around 3292 cm^{-1} related to stretching of the O—H bond is very broad for the initial complex of $\text{MgCl}_2 \cdot 3.4\text{EtOH}$, and after the treatment with alkylaluminum, the OH peak intensity is reduced considerably, and it is shifted to a higher frequency value (3473 cm^{-1}). In addition, the spectrum of the modified support demonstrates the presence of new bands, *inter alia* at 1166 cm^{-1} , which result from the presence of the Al—CH₂ group [TWI CH₂(Al)].

Immobilization of the vanadium complex on the magnesium support was carried out by comilling of catalyst components in the mixture of two solvents: toluene and hexane. Coloration of the reaction mixture changed during that process: from dark green to dark olive green. After separation, the light olive green solid and almost colorless filtrate were obtained, the latter indicating quantitative in practice immobilization of the complex. The aluminum and vanadium contents in the supported vanadium precatalyst, as determined by the atomic absorption spectroscopy, were 0.0415 g Al/g cat (1.54 mmol Al/g cat) and 4.10 mg V/g cat, i.e., 0.081 mmol of vanadium per gram of the supported precatalyst.

In the FTIR spectrum of the obtained supported vanadium catalyst (Fig. 2, curve 4), the absorption band at around 1649 cm^{-1} for the group N=C is visible; that did not change

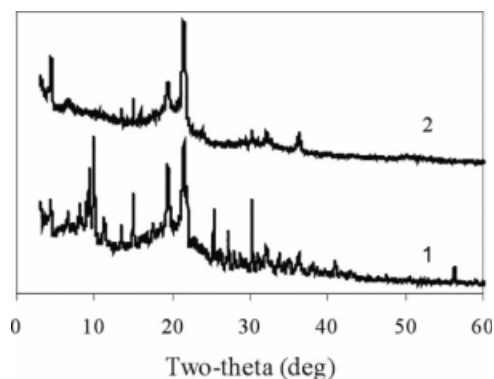


FIGURE 1 XRD patterns of $\text{MgCl}_2 \cdot 3.4\text{EtOH}$ (1) and the magnesium adduct treated with Et_2AlCl (2).

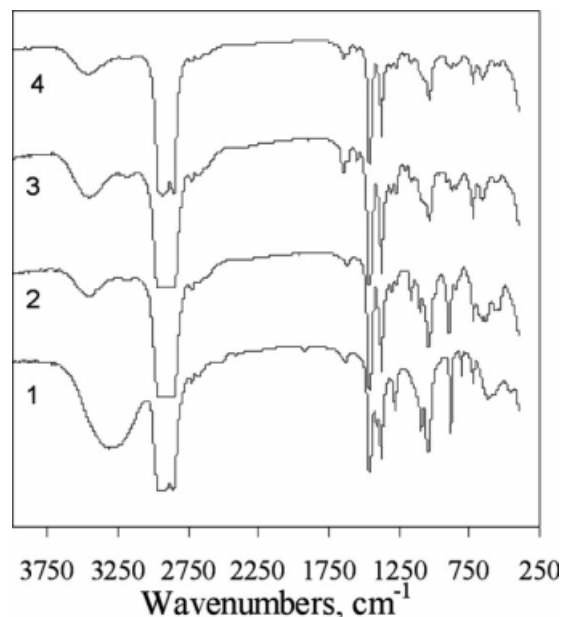


FIGURE 2 The FTIR spectra of $\text{MgCl}_2 \cdot 3.4\text{EtOH}$ (1), magnesium adduct treated with Et_2AlCl (2) supported titanium catalyst (3), and supported vanadium catalyst (4).

its location in practice with reference to the free complex (1653 cm^{-1}). Equivalent results were obtained for the analogous titanium complex which was immobilized on the same carrier (Fig. 2, curve 3). That may suggest that no chemical reaction takes place between the carrier and the complex. These results are similar to those presented for the salen complex of zirconium when immobilized on silica,¹⁹ for which—on the basis of FTIR measurements and the Cl/Zr ratio—it was also found that the deposition of the salen complex on silica left the catalytic component intact. This situation is different from that for the metallocene catalysts, for which immobilization on the silica supports was found to take place as a result of elimination of one or more ligands such as halides or alkoxides at the ratio of 1:1, in the reaction with hydrogen atoms from the silanol groups in the support.²⁰

SEM micrographs of the supported vanadium precatalyst and, for comparison titanium precatalyst obtained by immobilization of the titanium complex with the same structure on the same support, are shown in Figure 3. It is visible that the shapes for both catalyst particles are rather regular although not spherical, and that the surfaces of those particles are porous. The BET surface area and the pore volume for the titanium precatalyst, as it was found earlier,¹⁴ are $20.7\text{ m}^2/\text{g}$ and 0.11 mL/g , respectively.

Ethylene Polymerization Studies

Ethylene polymerization, with the use of the prepared supported vanadium catalyst, was carried out in the presence of various alkylaluminum compounds, at standard temperature of $50\text{ }^\circ\text{C}$. Each test took 30 min and the results are shown in Table 1, which also contains the results of the experiment

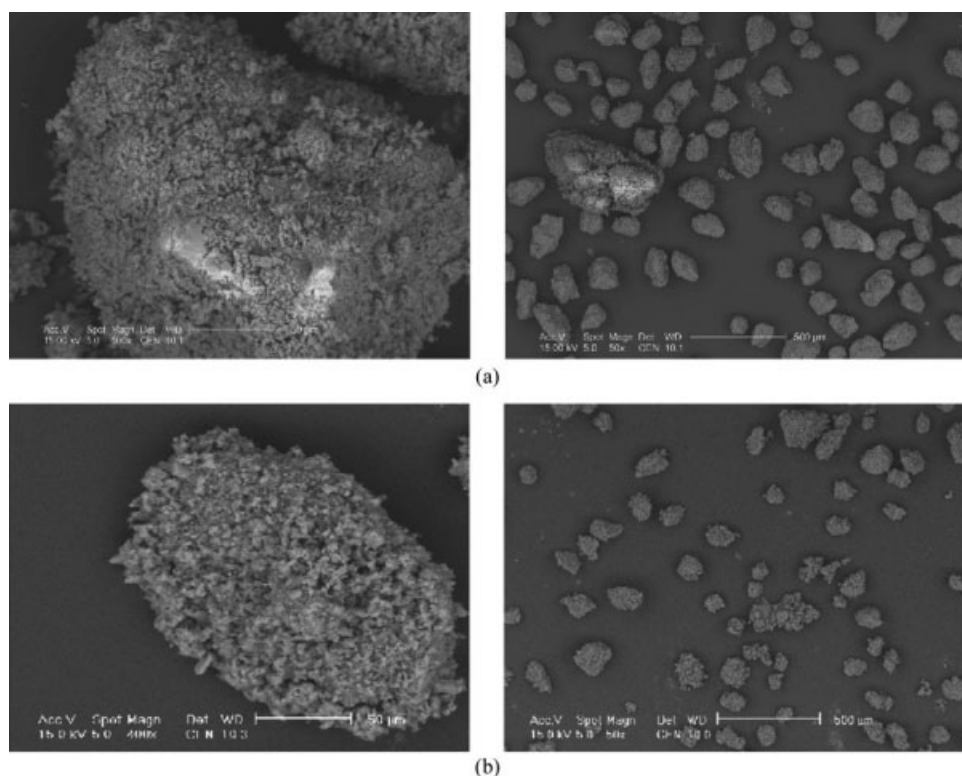


FIGURE 3 SEM images of (a) supported titanium precatalyst (magnification $\times 500$ and $\times 50$) and (b) supported vanadium precatalyst (magnification $\times 400$ and $\times 50$).

which was carried out earlier and in which the nonsupported vanadium complex was employed.¹⁰ The activities of unsupported salen-type vanadium complex, alike for other vanadium complexes,^{4,8} turned out highest when in conjunc-

tion with partially chlorinated aluminum alkyl compounds. EtAlCl_2 was the best activator in our case and the activity was around 21 kg/(g V 0.5 h) (Table 1). Notable changes in the catalytic activity were observed when the vanadium

TABLE 1 Results of Ethylene Homopolymerizations with Unsupported and Supported Vanadium Catalyst

Run	Activator	Temp. ($^{\circ}\text{C}$)	Yield (g)	Activity [kg/(g V 0.5 h)]	M_w (kg/mol)	M_w/M_n	$x\text{CH}_3/1000 \text{ C}$	T_m ($^{\circ}\text{C}$)	χ (%)
A1 ^a	EtAlCl_2^b	30	6.73	21.0	685	8.4	0.1	137.8	65.3
A2 ^a	Et_2AlCl^c	30	2.38	0.7	nd	nd	0.8	139.0	64.7
1	Me_3Al	50	3.607	44.0	2,750	10.7	0.2	136.8	51.9
2	Et_2AlCl	50	0.528	6.4	1,680	10.4	0	136.7	55.4
3	EtAlCl_2	50	1.033	12.6	1,580	10.9	nd	nd	nd
4	Et_3Al	50	1.042	12.7	2,290	14.5	0	136.9	51.6
5	MAO	50	5.530	67.4	nd	nd	0.2	136.8	56.1
6	MAO	20	1.258	15.3	3,010	10.8	0	136.5	50.7
7	MAO	30	2.434	29.7	2,740	14.2	0	135.5	48.8
8	MAO	40	3.343	40.8	nd	nd	0	136.0	46.3
9	MAO	60	6.864	83.7	2,570	10.7	0.2	136.7	51.2
10	Me_3Al	20	1.901	23.2	4,190	13.2	0.2	137.9	46.4
11	Me_3Al	30	3.316	40.4	nd	nd	nd	138.3	43.1
12	Me_3Al	40	3.470	42.3	3,705	14.1	nd	136.6	50.1
13	Me_3Al	60	4.472	54.5	nd	nd	0.3	138.7	44.9

Polymerization conditions: ethylene pressure 5 atm., polymerization time 30 min, amount of catalyst 0.0200 g, amount of common alkylaluminum compounds 7.6 mmol, amount of MAO 10.6 mmol, hexane 150 mL.

^a Results from ref. 1.

^b Amount of EtAlCl_2 3.6 mmol, amount of vanadium complex 0.006 mmol.

^c Amount of Et_2AlCl 7.9 mmol, amount of vanadium complex 0.07 mmol.

complex was immobilized on the magnesium carrier. Although the catalytic activity of the supported vanadium catalyst, alike that of its unsupported equivalent, was highly dependent on the type of the cocatalyst employed, yet the efficiency of activators changed (Table 1). Halogen-containing alkylaluminum compounds did not make suitable activators for the supported catalyst; the highest activity was obtained in the presence of Me_3Al , and MAO was a particularly effective activator—it gave 67.4 kg/(g V 0.5 h) (Table 1, run 5). A similar observation was made earlier for the titanium analogue; its efficiency profile looked like that: $\text{Me}_3\text{Al} > \text{MAO} > \text{Et}_3\text{Al}$, and it was practically inactive in conjunction with Et_2AlCl , i.e., with the best activator for the unsupported complex.¹⁴ Hence, the immobilization of both titanium and vanadium complexes on the magnesium carrier seems to produce a new type of active sites in the catalytic system.

The vanadium complex in the unsupported form gives linear polyethylene with high molecular weight, i.e., 685 kg/mol (Table 1, run A1). The immobilized system produces the polymer with similar properties, e.g., linear polyethylene with virtually no branching and high molecular weight. However, the available molecular weight values are clearly higher. The polymer obtained with Me_3Al as a cocatalyst at 50 °C has M_w equal 2750 kg/mol (Table 1, run 1). Moreover, the polymers synthesized over the supported catalyst feature a wider distribution of molecular weights than the polymers obtained from the unsupported system (from 10.4 to 14.5). The molecular weight distribution curves for those polymers are not clearly monomodal; shoulders can be seen for all samples. The effect of support, as observed earlier, in the analogue titanium system on polyethylene molecular weight was similar.¹⁴ It should also be mentioned, however, that the nature of the metal center influences the molecular weight of polyethylenes produced. The vanadium catalyst gives polyethylenes with clearly higher molecular weight than the titanium one does (for polymers produced at 50 °C, with the use of vanadium and titanium supported complexes activated by Me_3Al , the values of M_w reach 2750 and 969 kg/mol,¹⁴ respectively). That effect of the central atom was described for other types of catalysts which contained titanium or vanadium as their metal centers.²¹

The effect of cocatalyst on particle size distribution in polyethylene obtained with the supported vanadium catalyst is similar to that observed for polymers which were synthesized with the use of the analogous supported titanium catalyst. Polyethylene with high grain sizes is obtained for the use of the trialkylaluminum compound as the activator; the fraction with grains over 2 mm is dominant (about 70 wt %) independently on the reaction temperature. The polymer synthesized with MAO as the activator is characterized by definitely lower grain sizes, and the span of those sizes is relatively wide. In this case, the fractions with the average particle size of 0.4 mm or 0.3 mm is dominant.

Effect of Polymerization Temperature and Reaction Time

Usually, the catalysts based on the vanadium compound are more active at lower polymerization temperatures.^{3,22} That

is also applicable to the unsupported salen-type vanadium complexes investigated by us—they show the maximum activity at 30 °C.¹⁰ To determine whether the supported vanadium catalyst is more resistant to higher temperatures and whether the temperature changes affect molecular weights of resultant polymers, the ethylene polymerization tests were carried out at temperatures within 20–60 °C, with the use of the best cocatalysts, i.e., Me_3Al and MAO. It is immediately obvious from the results presented in Table 1 that immobilization of the vanadium complex results in higher thermal stability of the species generated on the support surface after activation with the cocatalyst; the highest activity was obtained at 60 °C for both cocatalysts. The activity of the supported vanadium catalyst increased with the rise in the polymerization temperature from 20 °C to 60 °C, from 23.2 kg/(g V 0.5 h) to 54.5 kg/(g V 0.5 h), and from 15.3 kg/(g V 0.5 h) to 83.7 kg/(g V 0.5 h) for Me_3Al and MAO cocatalysts, respectively. The higher activity may also result from the higher propagation rate at higher temperatures. On the basis of the results obtained, from the Arrhenius plot, the activation energy values for the MAO and Me_3Al activators were estimated at 46 and 26 kJ/mol, respectively. For the need of comparison, the data provided in ref. 14 were utilized to find the activation energy value for the equivalent supported titanium catalyst—it is equal to 92 kJ/mol for the Et_3Al activated system.

Apart from a notable increase in the catalytic activity at the increased reaction temperature, the molecular weight of the polymer is considerably reduced, too, from 3010 kg/mol at 20 °C to 2570 kg/mol at 60 °C for the polymer synthesized in the presence of MAO, and from 4190 kg/mol at 20 °C to 2750 kg/mol at 50 °C when Me_3Al is used as the cocatalyst. The higher chain transfer rates at higher temperatures can be responsible for this effect.

To better understand the catalyst deactivation process, we undertook experiments with the use of a flow-meter which allowed us to follow the changes in the catalyst productivity and in the polymerization rate over time. The results for polymerizations conducted at 60 °C in the presence of the catalyst activated by MAO and by Me_3Al are given in Figure 4. Both kinetic curves are of decay type. However, decline in the polymerization rate is rather moderate at the early stages of polymerization (up to 30 min of polymerization), and then it becomes relatively very slow. Both the catalytic systems still exhibit good activity after 70 min of polymerization. In contrast to the vanadium catalyst, the analogue supported titanium complex was found¹⁴ to possess the accelerating type kinetics: the initial increase in the activity was observed, and then the activity remained stable in practice.

Ethylene/1-Octene Copolymerization

Copolymers of ethylene with higher 1-olefin, which are known as LLDPE resins, are produced commercially nowadays. The catalytic system which is involved in the production of such polymers is crucial for incorporation of comonomer, for distribution of short chain branches in the polymer structure, for molecular weight, and for its distribution,

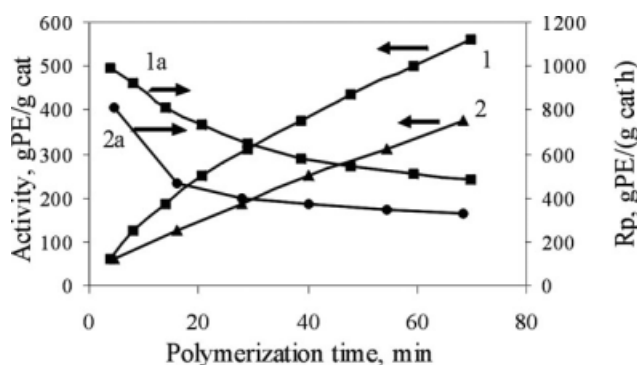


FIGURE 4 Effect of polymerization time on activity of supported vanadium catalyst activated by MAO (1) and Me_3Al (2) and polymerization rate (1a and 2a, respectively). Polymerization conditions: 60 °C, ethylene pressure 5 atm, amount of catalyst 0.0200 g, amount of cocatalyst 10.6 mmol of MAO, 7.6 mmol of Me_3Al .

which results in various polyethylene properties such as crystallinity, melting point or density. Despite the importance of such types of polymers, the literature reports on copolymerization of ethylene and higher 1-olefins over postmetallocene systems are relatively few. Hence, we decided to verify the copolymerization ability of the supported vanadium catalyst and, for comparison, for its titanium counterpart. The investigated supported vanadium catalyst turned out a good catalyst not only for ethylene homopolymerization but also for copolymerization with 1-octene. As shown in Table 2, it exhibits a relatively high catalytic activity in copolymerization, yet clearly inferior to that for ethylene homopolymerization (43 kg/(g V 0.5 h) at comonomer concentration of 0.1 mol/L and 83.7 kg/(g V 0.5 h) for homopolymerization, respectively). Moreover, the activity clearly decreases with the increasing comonomer concentration. At the highest comonomer concentration in the reaction environment, activity of the vanadium catalyst does not exceed 17 kg/(g V 0.5 h) (Table 2, run 20). The initial comonomer concentration

also influences comonomer incorporation into the polymer chain, which increases with the increasing comonomer concentration to reach the value of 4.45 mol % at 1.82 mol/L. Consequently, the polymer properties change: the melting point goes down (from 136.7 at 0 mol/L to 123.9 at 1.82 mol/L) and so does crystallinity (from 48.3% down to 33% for the comonomer concentration changed from 0.1 mol/L to 1.82 mol/L). The polymer molecular weight is reduced, too. These changes in the molecular weight may be attributed to the effects of the higher olefin as a chain transfer agent. The molecular weight distribution is wide, just alike for ethylene homopolymers.

The nature of the transition metal is known to have a significant impact on the performance of the catalytic system. Hence, for comparison, we made a series of copolymerization experiments with the equivalent titanium-based catalyst. We checked its activity in copolymerization in conjunction with Me_3Al (the best activator for the titanium catalyst), at standard reaction conditions, the same as for the vanadium catalyst. In ethylene/1-octene copolymerization, alike in ethylene homopolymerization, the titanium catalyst was more active than the vanadium one; for example, at the comonomer concentration of 0.4 mol/L their activities were 138.5 kg/(g Ti 0.5 h) and 30.2 kg/(g V 0.5 h), respectively. The activity of the titanium catalyst, similarly to the vanadium one, declined when the comonomer concentration was increased (Table 3). However, that decline in relation to homopolymerization was definitely lower than observed for the vanadium catalyst. The activity of the titanium catalyst at the highest comonomer concentration was lower by about 30%, while the vanadium catalyst reduced its performance by 80%. Yet, the titanium catalyst produced copolymers with considerably lower comonomer incorporation. The highest comonomer concentration, 1.82 mol/L, allowed to obtain the copolymer with the comonomer content of 1.35 mol % only. It is generally observed phenomenon that comonomer incorporation decreases by changing catalyst from vanadium to titanium-based one.²³ The low level of 1-alkene incorporation results

TABLE 2 Results of Ethylene/1-Octene Copolymerizations with Supported Vanadium Catalyst Activated by MAO

Run	C_8H_{16} (mol/L)	Yield (g)	Activity [kg/(g V 0.5h)]	M_w (kg/mol)	M_w/M_n	1-Octene Content in the Copolymer (% mol)	T_m (°C)	χ (%)
9	0	6.864	83.7	2,570	10.7	0	136.7	51.2
14	0.10	3.525	43.0	nd	nd	0.75	130.3	48.3
15	0.21	2.628	32.0	2,426	13.5	0.70	129.3	46.2
16	0.40	2.477	30.2	nd	nd	0.91	128.1	47.4
18	0.75	1.835	22.4	2,014	12.7	1.42	nd	nd
19	1.34	1.458	17.8	nd	nd	3.39	123.6	41.4
20	1.82	1.369	16.7	848	9.8	4.45	123.9	33.0

Polymerization conditions: ethylene pressure 5 atm., polymerization time 30 min, temp. 60 °C, amount of catalyst 0.0200 g, amount of MAO 10.65 mmol, hexane 150 mL.

TABLE 3 Results of Ethylene/1-Octene Copolymerizations with Supported Titanium Catalyst Activated by Me₃Al

Run	C ₈ H ₁₆ (mol/L)	Yield (g)	Activity [kg/(g Ti 0.5h)]	1-Octene Content in the Copolymer (% mol)	T _m (°C)	χ (%)
21	0	16.865	160.5	0	138.4	56.1
22	0.10	17.705	166.9	0.39	133.1	50.1
23	0.21	16.056	151.5	nd	133.2	52.6
24	0.40	14.681	138.5	0.72	131.9	55.6
27	1.34	14.021	132.3	1.22	130.2	46.4
28	1.82	11.794	111.3	1.35	130.1	45.0

Polymerization conditions: ethylene pressure 5 atm., polymerization time 30 min, temp. 60 °C, amount of catalyst 0.0200 g, amount of Me₃Al 7.6 mmol, hexane 150 mL.

in lower changes in the polymer properties, i.e., in melting point and crystallinity (Table 3). In the case of the titanium catalyst, its ability to homopolymerize 1-octene was verified as well. However, no polyoctene was produced under assumed conditions, i.e., 0.01 g of catalyst, 5.8 mmol of Me₃Al, 60 °C, 120 min, and 18 mL of 1-octene.

CONCLUSIONS

We successfully immobilized and activated the vanadium complex having the tetradentate [O,N,N,O]-type ligand, which was used in ethylene homopolymerization and in its copolymerization with 1-octene. The presence of the magnesium chloride support had a considerable effect on the catalytic activity of the vanadium complex and on the efficiency of the cocatalyst (MAO and EtAlCl₂ are the best activators for supported and unsupported precatalysts, respectively). These findings, together with the changes in the molecular weights of the obtained products, clearly indicate the significant role of the support in generation of the active sites in the supported catalyst. The new sites are much more resistant to deactivation at higher temperatures than the sites which are present in an unsupported system.

The nature of the metal center (vanadium or titanium) in the supported catalyst influences its activity, ability to incorporate 1-alkene into the polymer chain, and the molecular weight of the polymer product. We found the vanadium catalyst less active than its titanium counterpart, however, the former being more efficient in incorporating the comonomer and giving polyethylene with higher molecular weights. Moreover, the supported vanadium and titanium catalysts differ from each other in the polymerization kinetic profiles, i.e., they exhibit the decay and accelerating type kinetics, respectively.

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