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Copolymerization of ethylene with higher 1-olefins over vanadium catalyst supported on Al(*i*-Bu)$_3$ modified magnesium carrier

Summary — Copolymerization of ethylene and higher 1-olefin over supported vanadium catalyst was studied. $VOCl_3$ after immobilization on the magnesium carrier [$MgCl_2(THF)_2$ modified with Al(*i*-Bu)$_3$] and after activation with Et_2AlCl was used as a catalytic system. The effects of the type of comonomer (1-hexene, 1-octene, 1-decene or 1-dodecene) and its concentration in the reaction medium on the yield of copolymerization, on incorporation of comonomer, and on some properties of the reaction products (molecular weight and its distribution, melting point, crystallinity) were investigated. The findings were compared to those available from analogous studies which had been carried out earlier with the use of the same catalyst immobilized on an unmodified magnesium complex.

Key words: copolymerization, ethylene, 1-olefin, vanadium catalyst, magnesium carrier, modification, organoaluminum compounds.

KOPOLIMERYZACJA ETYLENU Z WYŻSZYMI 1-OLEFINAMI WOBEC KATALIZATORA WANADOWEGO OSADZONEGO NA MODYFIKOWANYM ZA POMOCĄ Al(*i*-Bu)$_3$ NOŚNIKU MAGNEZOWYM

Streszczenie — Badano proces kopolimeryzacji etylenu z wyższymi 1-olefinami (C_6—C_{12}) wobec katalizatora wanadowego ($VOCl_3$) immobilizowanego na nośniku magnezowym $MgCl_2(THF)_2$ modyfikowanym z zastosowaniem Al(*i*-Bu)$_3$. W charakterze aktywatora nośnikowego prekatalizatora wanadowego zastosowano Et_2AlCl. Stwierdzono, że aktywność takiego układu katalitycznego jest porównywalna z aktywnością katalizatora z prekursorem wanadowym osadzonym na niemodyfikowanym nośniku magnezowym. Zaobserwowano także, że wprowadzenie komonomeru do środowiska reakcji powoduje niewielkie zmniejszenie wydajności procesu w porównaniu z homopolimeryzacją etylenu, postępującą w miarę wzrostu stężenia komonomeru w środowisku reakcji. Dodatkowo zauważono, że udział tego negatywnego zjawiska jest tym większy im krótszy jest węglowodorowy łańcuch komonomeru (rys. 1). Stopień wbudowania komonomeru do łańcucha polietylenu także zależy zarówno od stężenia, jak i od długości łańcucha wyższej olefiny i maleje w szeregu: 1-heksen > 1-okten > 1-decen > 1-dodecen (rys. 2 i tabela 1). Należy podkreślić, że immobilizacja katalizatora wanadowego na wspomnianym nośniku modyfikowanym związkiem glinoorganicznym polepsza efektywność wbudowywania komonomeru (zwłaszcza o dłuższym łańcuchu) do PE w porównaniu z efektywnością takiego samego katalizatora zakotwiczonego na niemodyfikowanym kompleksie $MgCl_2(THF)_2$. Można zatem przypuszczać, że modyfikacja $MgCl_2(THF)_2$ związkiem glinoorganicznym prowadzi do zmiany charakteru centrum aktywnego, które — bardziej wówczas oddalone od powierzchni nośnika — staje się łatwiej dostępne dla cząsteczki komonomeru. Scharakteryzowano również wpływ rodzaju i zawartości komonomeru na zmianę ciężaru cząsteczkowego, temperatury topnienia i stopnia krystaliczności produktów (rys. 3 i 4).

Słowa kluczowe: kopolimeryzacja, etylen, 1-olefina, katalizator wanadowy, nośnik magnezowy, modyfikacja, związki glinoorganiczne.

MODIFICATION OF MAGNESIUM CARRIER WITH ORGANOALUMINUM COMPOUNDS FOR CATALYTIC SYSTEM USED IN HOMO- AND COPOLYMERIZATION OF OLEFINS

It has already been demonstrated that the activities of the supported organometallic catalysts in the olefin polymerization processes as well as the properties of the reaction products are to a large extent dependent on the support and catalyst preparation method, inclusive of chemical modification of the support most of all with an organoaluminum compound. Such effects have been observed as well for the Ziegler—Natta systems and for metallocene catalysts, which have been anchored on oxide supports and on magnesium chloride [1—3].

The effect of carrier modification on the catalyst performance in the ethylene polymerization process was demonstrated for Ziegler—Natta catalysts, mostly the ones consisting of the titanium precursor and the magnesium support [1, 2]. It was presented in [1] that the titanium catalytic system utilizing a bimetallic support obtained by co-milling of $MgCl_2(THF)_2$ with the equimolar amount of Et_2AlCl showed a higher activity than its counterpart supported on an unmodified magnesium carrier. It is known [2, 4—6] that modification of the support with an organoaluminum compound may remove some part of THF from the support and thus productivity of the catalyst may be changed, and the change in activity was dependent both on the type(s) of monomer(s) employed in copolymerization and on THF elimination from the system. In the case of the catalyst $TiCl_3(1/3AlCl_3)/3MgCl_2/THF$ it was reported that the rate of ethylene homopolymerization initially increased with THF removal and then it decreased, while the rate of propylene polymerization increased in this time [2]. The activity in copolymerization mostly decreases with THF removal.

The results of copolymerization of ethylene and 1-butene with the use of $TiCl_3 \cdot 1/3AlCl_3/MgCl_2/THF$ or $TiCl_3 \cdot 1/3AlCl_3/MgCl_2/THF/AlEt_2Cl$ catalyst activated by $AlEt_3$ were described in [4]. The latter catalyst, modified with $AlEt_2Cl$ before its specific activation by $AlEt_3$, displayed a better activity in the copolymerization process in relation to an unmodified system. The polymerization rate profile consisted of a two step activation curve, which can be explain by the presence of at least two kinds of active species, namely the pre-activated sites and the sites activated with $AlEt_3$ at the later stage. Moreover, this catalyst was more active towards 1-butene then the catalyst without any modification with Et_2AlCl. The contents of 1-butene units in copolymers obtained under the same polymerization conditions, for modified and unmodified catalysts, amounted to 8.5 and 5.1 mol %, respectively.

It is frequently stressed for metallocene catalysts that modification of the carrier with an organoaluminum compound increases the anchoring degree of a transition metal on the carrier surface. Conte and Marques found out [7] that after inmiobilization of Cp_2ZrCl_2 catalyst on methylaluminoxane (MAO) pretreated $MgCl_2$, its activity in olefin polymerization was higher than that for the catalyst which had not been subjected to any pretreatment. They concluded that the enhancement in the activity was related to the increase in the amount/number of active centres fixed.

$Et(IndH_4)ZrCl_2$ immobilized on silica previously modified with different chemical compounds, *inter alia* with MAO, was studied in the copolymerization of ethylene with propylene [8]. The MAO-modified system also in that case gave the higher Zr loading then the catalyst supported on bare silica, though the last one was slightly more active in the copolymerization process. Additionally, the system pretreated with MAO gave higher propylene incorporation.

It was also stated in [9] that silica/MAO and silica supported zirconocenes differed slightly in their ability to incorporate the comonomer into the growing polymer chain. The polymers obtained with the non-modified silica support had lower comonomer contents. The modification of the support, however, had no effect on molecular characteristics of the polymerization products; the molecular weight distribution was narrow for all copolymers, indicating a uniform catalytic site.

Authors of [9] investigated also the effect of support treatment (silica or MAO-pretreated silica) on ethylene and 1-hexene copolymerization in the presence of hafnocene catalysts. They found that the chemical composition distribution (*CCD*) of copolymers can be significantly altered by the way the support was treated: the unimodal *CCD* was obtained for copolymers synthesized with use of Cp_2HfCl_2 supported on silica, while bimodal *CCD* resulted when MAO-modified silica was used as a support. This can be linked to the presence of more then one active site type during polymerization.

Our earlier research [5, 10] covered the copolymerization process of ethylene and 1-hexene with the use of $MgCl_2(THF)_2$ supported Cp_2ZrCl_2/MAO catalyst which had been modified with various organoaluminum compounds (MAO, Et_2AlCl, Me_3Al, $i\text{-}Bu_3Al$). Modification of the carrier and the type of the modifying agent were found to affect productivity of the catalyst and molecular weight of the copolymer obtained, but they did not influence the composition of this product.

We decided to extend our research and to verify whether carrier modification with an organoaluminum compound affected the course of ethylene copolymerization in the presence of a typical Ziegler—Natta catalyst or not. We had already studied the copolymerization process of ethylene and higher 1-olefins in the presence of the vanadium catalyst ($VOCl_3/Et_2AlCl$) anchored on $MgCl_2(THF)_2$ [11, 12]. In this study, the magnesium carrier prepared by modification of $MgCl_2(THF)_2$ complex with $Al(i\text{-}Bu)_3$ was used for immobilization of $VOCl_3$ precursor. The pre-catalyst obtained was employed after its activation with Et_2AlCl in homopolymerization of ethylene and in copolymerization of ethylene with higher 1-olefins (1-hexene, 1-octene, 1-decene or 1-dodecene). The findings were then compared with those obtained earlier for the catalyst anchored on the unmodified $MgCl_2(THF)_2$ complex [11, 12].

EXPERIMENTAL

All chemical operations described below were conducted under nitrogen atmosphere using the standard Schlenk and glove box techniques.

Materials

Ethylene, hexane and higher 1-olefins were purified and dried according to the standard method (*e.g.* [5, 10]). $VOCl_3$ and alkylaluminum compounds (Aldrich) were used as received.

Magnesium support modification

Synthesis of the magnesium support $MgCl_2(THF)_2$ and its modification with organoaluminum compound [Al(*i*-Bu)$_3$] followed the procedure described in detail in [5, 13]. The reaction of the magnesium complex and the organoaluminum compound (Mg/Al = 1/2.5 mol/mol) was conducted in toluene for 3.5 h, and the reaction temperature was increasing from 20 to 80 ^oC. The solid product was then filtered off and washed a few times with hexane.

Synthesis of vanadium pre-catalyst

The vanadium pre-catalyst was obtained by milling of $VOCl_3$ together with the modified magnesium carrier (about 2 mmols V per 1 g carrier) in hexane, at room temperature, for 20 h. The solid product was then filtered off, washed several times with hexane and dried. The transition metal content in the supported pre-catalyst was determined by the atomic absorption spectroscopy (AAS) method, after previous mineralization of the sample; the amount of V anchored on the carrier surface was 22.4 mg/1 g pre-catalyst. For polymerization processes the suspension of the supported vanadium catalyst in hexane was used.

Copolymerization

The copolymerization reactions were carried out at 50 ^oC in a 1 dm^3 reactor equipped with a mechanical stirrer. The reactor was filled with hexane (0.7 dm^3) and the co-catalyst ($AlEt_2Cl$, 20 mmol), 1-olefin (in case of copolymerization) and the pre-catalyst (0.06 g) were charged there. The copolymerization reaction was initiated by the introduction of ethylene. The monomer pressure was kept constant (0.5 MPa) during polymerization by the continuous addition of ethylene. The reaction was stopped by the introduction of the acidic solution of methanol. The polymer was subsequently filtered off, washed with methanol and dried under vacuum.

Methods of testing

The polymers characterization study (co-monomer incorporation, molecular weight, molecular weight distribution, melting point and crystallinity) was carried out in the same way as reported in details in [5, 11].

The molecular weights and polydispersity indices ($PDI = \overline{M}_w/\overline{M}_n$) were determined by size exclusion chromatography (SEC), using a Waters instrument, model 150-C, equipped with a refractive index attachment. The average molecular weight values were found making use of the polystyrene calibration curve obtained for narrow *PDIs*.

The heat of fusion (ΔH_f) and melting temperature (T_m) were measured for the samples (which had been previously melted and recrystallized) with the use of a TA Instruments 2010 DSC calorimeter.

The comonomer incorporation degrees were determined by IR method (Philips PU 9800 FT-IR spectrometer), using $A^{1379}_{CH_3} / A^{1369}_{CH_2}$ absorbance ratios, which were obtained by separation of analytical bands [14].

RESULTS AND DISCUSSION

Activity of the studied vanadium catalyst, anchored on $MgCl_2(THF)_2$ modified with triisobutylaluminum, in homopolymerization of ethylene is about 47 kg PE per 1 gram of transition metal (1.13 kg PE/1 g catalyst), and it is comparable to the activity of the catalyst anchored on the unmodified carrier (about 53 kg PE/g V), when the comparable reaction conditions are provided [15]. Hence, unlike in the case of metallocene catalysts anchored on the same magnesium carrier which have been investigated earlier, modification of $MgCl_2(THF)_2$ exhibits no significant effect on the activity of the vanadium catalyst in ethylene homopolymerization.

When a comonomer is added to the reaction medium, the yield decreases as compared to the ethylene homopolymerization process (Fig. 1). That negative effect of a presence of higher olefin on the catalyst activity in ethylene copolymerization has been observed earlier by other authors [16—18], but the positive impact of a comonomer, in particular at low concentrations, on the catalytic activity has also been reported [19—22]. Our earlier studies with the use of $MgCl_2(THF)_2/VOCl_3/Et_2AlCl$ catalyst also confirmed that the presence of ole-

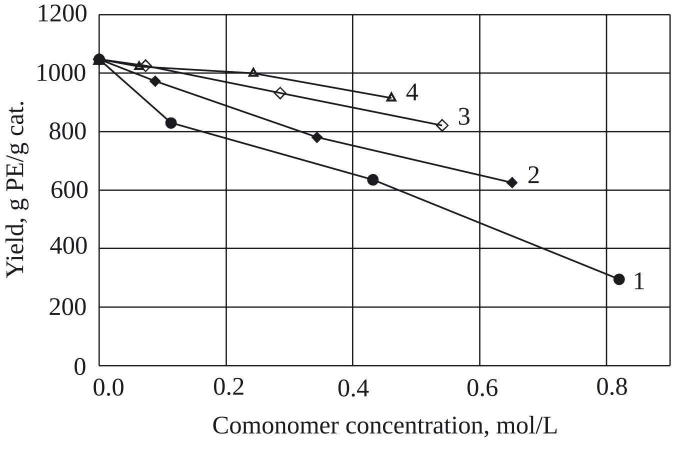


Fig. 1. Effects of comonomer type and concentration on catalyst activity (1 — 1-hexene, 2 — 1-octene, 3 — 1-decene, 4 — 1-dodecene)

fin in the reaction medium at a very low amount, *i.e.* about 0.005 mol/dm^3, activated the catalytic system. Higher concentrations of a comonomer, however, were responsible for a decline in the efficiency of the catalyst employed. In our present investigation, with the use of a catalyst immobilized on a modified magnesium support, we also found out that higher concentrations of olefins in the reaction medium would reduce the yield of copolymerization, irrespective of the type of a higher olefin added. However the effect of the size of the comonomer was clearly seen, namely the lowest drop in the process efficiency was observed for 1-dodecene being the biggest molecule. Those changes in the process yield may suggest that the growing chain length of the comonomer hinders its contact with the catalytic active site, and hence ethylene dominates in the reaction which improves the process yield. On the other hand, lower amounts of a high molecular weight comonomer are built-in to the polyethylene chain.

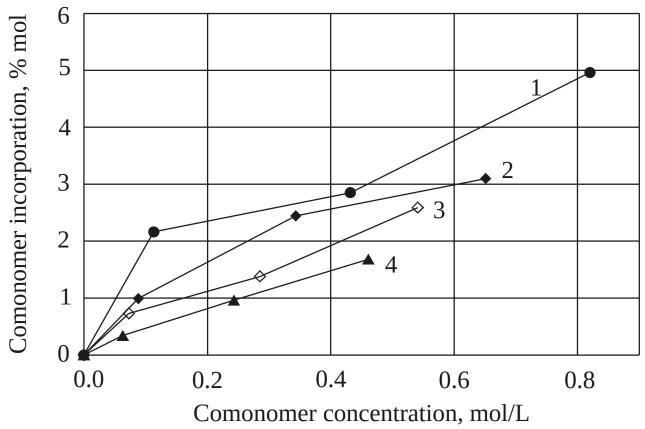


Fig. 2. Effects of comonomer type and concentration on the incorporation of 1-olefin into polyethylene chain (1 — 1-hexene, 2 — 1-octene, 3 — 1-decene, 4 — 1-dodecene)

Those conclusions comply with the investigation of the effects of the type and concentration of higher 1-olefin on the amount of comonomer built-in to the polymer chain; the findings from that investigation have been presented in Fig. 2. Incorporation of 1-hexene to the polyethylene chain (curve 1), at the same concentrations of comonomers in the reaction medium, is highest for the studied 1-olefins and the incorporation declines in the following sequence: 1-hexene > 1-octene > 1-decene > 1-dodecene.

The obtained data was also used to find the reactivity coefficients by the Fineman-Ross method. As the fraction of comonomer is relatively low in the copolymer (below 10 mol %), the simplified equation was adopted [23] which gave the reactivity coefficient for ethylene (r_E):

$$m_2/m_1 = (1/r_E)([M_2]/[M_1]) \quad (1)$$

where: m_1 — *molar fraction of ethylene in copolymer,* m_2 — *molar fraction of 1-olefin in copolymer,* $[M_1]$ — *concentration of ethylene in reaction medium at 50 °C,* $[M_2]$ — *concentration of 1-olefin in reaction medium.*

Table 1. Ethylene reactivity ratio (r_E) obtained for ethylene/1-olefin copolymerization in the presence of vanadium catalyst supported on Al(*i*-Bu)$_3$ modified MgCl$_2$(THF)$_2$ (A) or unmodified magnesium complex (B)

Catalyst	Comonomer			
	1-hexene	1-octene	1-decene	1-dodecene
A	46.5	54.6	56.8	71.9
B	66.7	—	120.7	232.0

The obtained values of ethylene reactivity coefficients in the process of copolymerization of ethylene and 1-olefin (catalyst A) have been presented in Table 1. As can be seen, the increasing chain length of 1-olefin gradually increases the value of r_E, which is in particular clear for 1-dodecene (for copolymerization with 1-decene value r_E is higher by about 20 % in relation to that for 1-hexene, and the growth of over 50 % is noted for copolymerization with 1-dodecene). Those figures mean a relative increase in the rate of building-in ethylene, while incorporation of a comonomer becomes less effective when the molecular size of the comonomer grows.

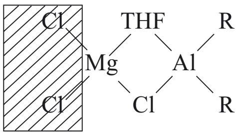
To make some comparative evaluation possible, Table 1 provides also ethylene reactivity coefficients, obtained earlier for the same catalyst which has been anchored on the unmodified complex of magnesium chloride with THF (catalyst B). Modification of the magnesium support with an organoaluminum compound apparently offers superior efficiency of comonomer incorporation (lower values of r_E are accompanied by increasing values of comonomer reactivity coefficients). The difference is especially high and advantageous for copolymerization of ethylene with spatially structured comonomers — 1-decene and 1-dodecene — where the difference is more than doubled for the first one and threefold for the other.

The similar advantageous result of carrier modification with an organoaluminum compound, *i.e.* improved efficiency of comonomer incorporation, was observed for the vanadium catalyst anchored on silica produced by sol-gel method and additionally modified with diethylchloroaluminum [24]. Galland *et al.* stated that low activities of supported metallocene catalysts in ethylene/1-hexene copolymerization could be attributed to the steric hindrance caused by the silica surface, which played the role of a huge ligand preventing the access of monomers to the catalysts' centers [25]. In this work it was also observed that supported catalyst let produce copolymers with lover comonomer incorporation then for their homogeneous counterparts.

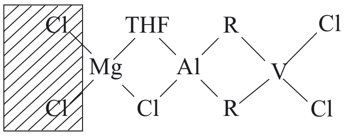
In turn in our work [5] we notice that heterogenization of metallocene catalyst on Al(*i*-Bu)$_3$ modified

$MgCl_2(THF)_2$ reduced a bit copolymerization ability of catalytic systems containing bigger ligands but efficiency of Cp_2ZrCl_2/MAO catalyst does not change after immobilization. We also found that incorporation ability of $VOCl_3/Et_2AlCl$ after immobilization on magnesium complex modified by triisobutylaluminum is pretty much the same (for example comonomer incorporation for unsupported and supported catalyst is equal 6.0 and 5.9, respectively) [26]. It thus appears that modification of a carrier with an organoaluminum compound induces a change in the nature of an active site; the site becomes more sensitive towards 1-olefin incorporation, especially in the case of comonomers with bigger molecules. One may expect as the reason, that the active site becomes carried further away from the carrier surface and thus it becomes easily accessible for a higher 1-olefin which is more spatially expanded.

It comes from the above that the organoaluminum compound may act as a spacer which moves active sites away from the carrier surface. In [27] the structure of active site formed as a result of reaction of the magnesium chloride complex modified by alkylaluminum and $TiCl_4$ is showed. The similar one can be proposed for vanadium catalyst:



(I)



(II)

When comonomer is introduced to the reaction medium, molecular weight of the product is reduced in comparison to homopolyethylene, and is further reduced for increasing concentration of comonomer (Fig. 3). The same effect of higher olefins on molecular weights of polymers was noted in many other reports [5, 11], irrespective of the type of the catalyst used, *i.e.* for metallocene and for Ziegler—Natta catalysts. That makes the evidence for the involvement of a comonomer in the polymer chain transfer reaction.

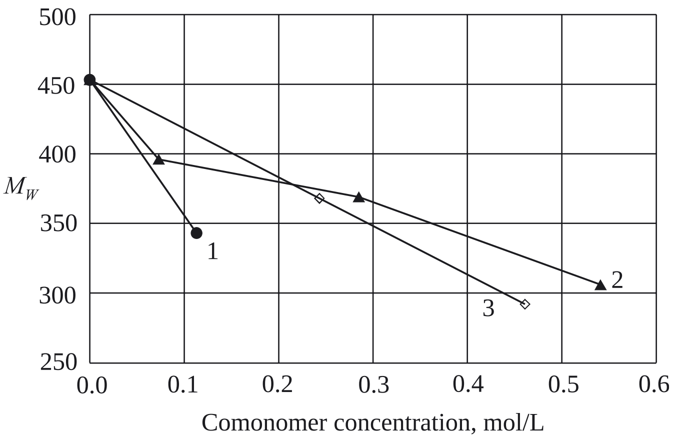


Fig. 3. Dependence of molecular weight of copolymer (M_W) on comonomer concentration in polymerization mixture (1 — 1-hexene, 2 — 1-decene, 3 — 1-dodecene)

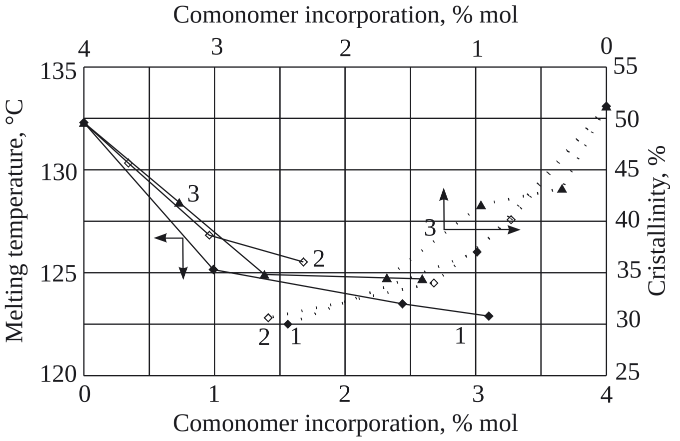


Fig. 4. Melting temperature and crystallinity of copolymers as functions of copolymer composition (1 — 1-octene, 2 — 1-decene, 3 — 1-dodecene)

The melting points and crystallinity of the copolymers obtained were also found to be dependent on the comonomer concentration in the reaction medium, and speaking more strictly on the comonomer fraction in the copolymer (Fig. 4.). Increasing amounts of built-in comonomer are responsible both for lower melting points and for lower contents of crystalline phase in all the products studied. What is worth mentioning is that the scope of those changes is hardly dependent on the type of higher olefin but also strongly dependent on the amount of comonomer incorporated.

CONCLUSION

Activity of the vanadium catalyst anchored on the $MgCl_2(THF)_2$ carrier modified with an organoaluminum compound was found in ethylene homopolymerization to be comparable with that of a system in which the vanadium precursor had been deposited on an unmodified magnesium carrier. It was also observed that the introduction of the comonomer resulted in a small decline in the process yield as compared to ethylene homopolymerization; that decline becomes more and more sharply outlined for the increasing comonomer concentration in the reaction medium. As was additionally noted, the scope of that negative phenomenon was growing for the shorter comonomer chains. The level of comonomer incorporation to the polyethylene chain was also dependent on the olefin concentration and on the hydrocarbon chain length of an olefin — it was decreasing in the following sequence: 1-hexene > 1-octene > 1-decene > 1-dodecene.

It should be stressed that the vanadium catalyst immobilized on a carrier modified with an organoaluminum compound was more efficient for incorporation of a comonomer to the polyethylene chain than the same catalyst which had been anchored on the unmodified $MgCl_2(THF)_2$ complex. That was in particular visible for comonomers with longer hydrocarbon chains. Hence, one may expect that the modification of $MgCl_2(THF)_2$ with an organoaluminum compound changes the nature of active sites. Those sites become more distant from the carrier surface and thanks to this they become more easily accessible for comonomer molecules in comparison to the system where no carrier modification was done. That difference is especially more evident for comonomers with longer hydrocarbon chains.

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