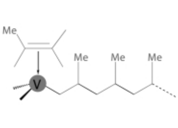
Homogeneous vanadium-based catalysts for the Ziegler–Natta polymerization of α-olefins



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Although their activity is often inferior to that of other systems, the use of vanadium-based catalysts in homogeneous Ziegler–Natta polymerizations allows the preparation of high-molecular-weight polymers with narrow molecular-weight distributions, ethene/α-olefin copolymers with high α-olefin incorporation, and syndiotactic polypropene. The main reason for the low activity of these catalysts is their deactivation during catalysis by reduction of active vanadium species to low-valent, less active or inactive species. We here present an up-to-date review of this area with particular emphasis on the attempts to improve catalyst performance and stability by the use of additives or ancillary ligands.

1 Introduction

Almost 50 years have past since the discovery of Karl Ziegler that ethene could be polymerized by transition metals under mild conditions. Since then a vast amount of research has been done to develop catalysts which have improved activities, give greater control over the polymers formed and can handle other (polar) monomers. The catalysts used have been based predominantly on early transition metals. However, in recent years an increasing number of reports about catalyst systems based on middle- and late-transition metals have appeared in the literature.[1] Even the main-group metal aluminium has been shown to produce polyethene under mild conditions.[2] The important lesson which can be learned from these findings is that it is not so much the metal, but the ligand system in combination with the metal which determines the outcome of the polymerization reaction. This was also the theme of our recent studies, which were directed to develop well-defined vanadium-based catalysts. Although the activity of vanadium-based catalysts is often inferior to that of other systems, their use allows the preparation of (1) high molecular weight polymers with narrow molecular weight distributions, (2) ethene/α-olefin copolymers with high α-olefin incorporation, and (3) syndiotactic polypropene.[3] One of the reasons for the low activity of

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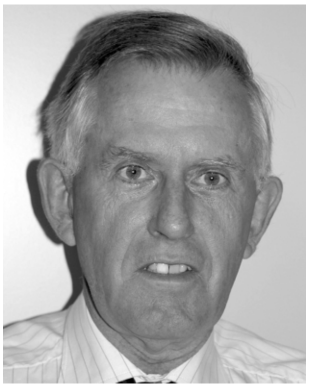
Henk Hagen



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vanadium-based catalysts is their deactivation during the polymerization process due to reduction of catalytically active vanadium species to low-valent, less active or inactive species. One way to overcome this problem would be the stabilization of the formal high oxidation state of the vanadium centre by ancillary ligands.

The use of vanadium to polymerize ethene was already reported in the late fifties by Carrick.[4] Since then many reports about the use of vanadium in olefin polymerization have appeared, although their number is relatively low compared to those concerning the group 4 metals titanium and zirconium. The main reasons are, apart from the low activity mentioned earlier, the often occurring paramagnetism and the instability of alkylvanadium compounds.

We here present an overview of the use of vanadium-based catalysts in the homogeneous Ziegler–Natta polymerization of olefins with particular emphasis on the attempts to improve the catalyst performance by the use of additives or ancillary ligands.

2 General

The catalytic system employed by Carrick[4] consisted of a mixture of VCl_4, $AlBr_3$ and R_3Al (R = Ph, *i*-Bu). The mixing of these compounds in hexane resulted in the formation of a clear pink solution which showed high activity in ethene polymerization at 60 °C and atmospheric pressure. Several other catalytic systems have also been employed. They were usually derived from a hydrocarbon-soluble vanadium compound (*e.g.* VCl_4, $VOCl_3$, $VO(OR)_3$, $VOCl(OR)_2$, $VOCl_2(OR)$ and $V(acac)_3$) and an alkylaluminium compound or an aluminium hydride derivative (*e.g.* R_3Al, R_2AlX, $R_3Al_2X_3$, $RAlX_2$, $HAlX_2{\cdot}B$ and $HXAlNR_2$ where R = alkyl, X = halogen, and B is a Lewis base).[5] Common features of these systems are: (1) The active species is a complex containing both vanadium and aluminium. (2) One of the components contains at least one halogen atom, unless the catalyst preparation and/or polymerization reaction is carried out in the presence of a halogen-containing hydrocarbon. (3) Divalent vanadium species formed by the reduction of the vanadium compound by the alkylaluminium compound are not active in the polymerization reaction. (4) The catalytic activity decays progressively during the polymerization, the kinetics of the decay being dependent on both the nature of the catalyst components and the conditions (*e.g.* temperature, concentration, solvent and presence of Lewis bases).

3 The stereospecific polymerization of propene

Due to the presence of a methyl group on every second carbon atom in the polymer chain of polypropene, the structure of this polymer can be described in terms of three basic forms: *i.e.* isotactic, syndiotactic and atactic (Fig. 1).

Both the physical and the mechanical properties of polypropene depend on the tacticity. Isotactic material has a combination of properties—high melting point, high mechanical strength as a consequence of crystallinity, good workability—that makes it the commercially most interesting form. Syndiotactic polypropene is a rubber-like material with potential applicability, while the atactic form is a useless sticky material. Soon after the discovery of Ziegler–Natta polymerization it was found that the use of solid-state catalysts in the polymerization of propene leads to the formation of polymers with high degrees of isotacticity. Syndiotactic polypropene was formed as well, but in very small quantities only.

In 1962, however, Natta *et al.* reported that the use of $V(acac)_3$ or VCl_4 in combination with a variety of dialkylaluminium compounds as co-catalysts yielded mainly syndiotactic polypropene.[6] This remarkable finding that a stereospecific polymer is formed starting from a non-chiral catalyst led to extensive studies of the polymerization mechanism.

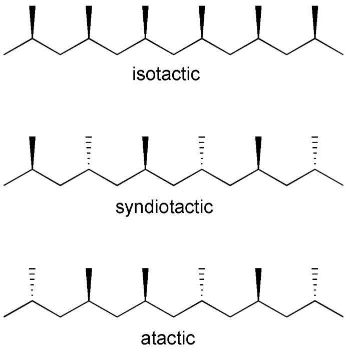


Fig. 1 The structure of isotactic, syndiotactic and atactic polypropene.

Zambelli *et al.* used EPR to show that the vanadium in the active species is trivalent and that the composition of this species is most probably VCl_2R.[7] They also stated that, as the structure of the co-catalyst has a large influence on the degree of syndiotacticity of the polymers obtained, it is very likely that the active species is bimetallic. Although to this moment the nature of the actual catalytic species is still unknown, Zambelli and Allegra have proposed a structural model which is consistent with all evidence found so far.[8] In this model, the active species is a five-coordinate vanadium(III) atom bearing three chlorides and the growing polymer chain (Fig. 2).

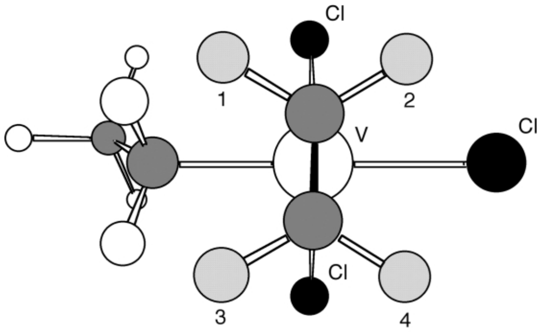


Fig. 2 Postulated structure of the active species and the four possible positions (1, 2, 3 and 4) of the methyl group upon coordination of propene.

Of the three chlorides two may be bridge-bonded to aluminium. The fifth coordination site is occupied by a side-on coordinated propene. Depending on the position of the methyl group of the propene, this coordination can take place in four ways. For the insertion of propene in the vanadium–carbon bond four orientations are conceivable, *viz.* 1.1, 1.2, 2.1 and 2.2 (Fig. 3).

Only two of these, *i.e.* stereoregular 1.1 and 2.2 insertion, may give rise to syndiotactic chain propagation. The propene insertion step is assumed to proceed *via* a concerted mechanism, in which the olefin rotates in such a way that the C=C bond becomes parallel to the Cl–V–C axis. This is assumed to be the step with the highest energy. Except for the 2.2 insertion, all insertion reactions have equal energies for each stereospecific insertion and therefore they yield stereo-random polymers. Once a 2.2 insertion has occurred it tends to persist because the energy for each following 2.2 insertion is much lower than for a 2.1 insertion. Also, with each new 2.2 insertion there is a preference for a syndiotactic insertion because of the steric interference of the growing chain with the olefin during the coordination process. Recently, Zambelli *et al.* used CF_3CH_2OD to terminate the vanadium salt/alkylaluminium

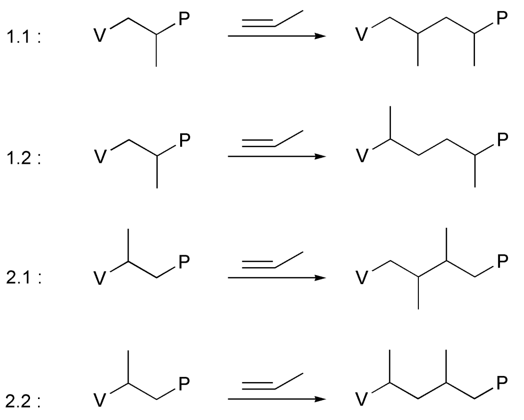


Fig. 3 Four possible insertion reactions in propene polymerization.

halide-catalyzed propene polymerization.[7] They showed that the propyl end-groups of the syndiotactic polypropene arise from termination and that indeed secondary insertion of propene is the only syndiotactic specific polymerization step.

Doi *et al.* found that the system originally used by Natta *et al.*, $V(acac)_3/Et_2AlCl$, not only gives syndiotactic polypropene, but that this system also has living character.[9] For a system to be 'living' three conditions have to be met, *viz.*: (1) the formation of propagation centres is effectively instantaneous, or its rate constant is not slower than that of the polymerization, (2) chain-transfer that limits molecular weight does not occur, and (3) irreversible termination with deactivation of the propagation centre does not take place. For the $V(acac)_3/Et_2AlCl$ system these criteria are satisfied and polymers with narrow molecular weight distributions (M_w/M_n = 1.05–1.20) are obtained. However, this occurs only at temperatures below −60 °C. At higher temperatures the number of polymer molecules increases with increasing reaction times, indicating the occurrence of chain-transfer reactions. A disadvantage of this acetylacetonate-based system is that only a few mole-percent of the vanadium present is active in the polymerization. The activity of the system could be increased by a factor three by the addition of anisole, while both the M_n and the syndiotacticity of the polymers were unaffected.[10] The higher activity was assigned to a participation of the anisole in the initiation reaction of $V(acac)_3$ with Et_2AlCl leading to an increase in the number of active vanadium centres. Since the polymer formed did not change with respect to both molecular weight and stereoregularity, it was assumed that the anisole did not affect the structure of the catalytic centre. Changing the ligand system from acetylacetonate to 2-methyl-1,3-butanedionate resulted in a further increase of activity. When the reaction using this ligand system was carried out at −40 °C all vanadium centres were active.[11]

Doi and Keii proposed a model for chain propagation based on a tetracoordinate V^{3+} as the active centre (Fig. 4).[12] The vanadium is bonded to a bidentate acetylacetonate, a chloride and an alkyl ligand while the chloride is also bonded to a dimeric dialkylaluminium chloride. Upon propene coordination, the active centre becomes pentacoordinate. In such a structure, regulation of the reactivity, regiospecificity and syndiotacticity is possible by varying the aluminium complex, which is bonded to the vanadium centre, as it influences both the electronic and geometrical features of the vanadium–carbon bond.

Due to the living character of the $V(acac)_3/Et_2AlCl$ system, it can also be used to prepare well-defined block-copolymers. The addition of a small amount of ethene after a certain time during the polymerization of propene resulted in the formation of a block consisting of a random ethene/propene copolymer. After the ethene had been consumed, the catalytic system continued to homopolymerize propene, thus leading to a well-defined P–R–P triblock copolymer with a polydispersity of approximately 1.25.

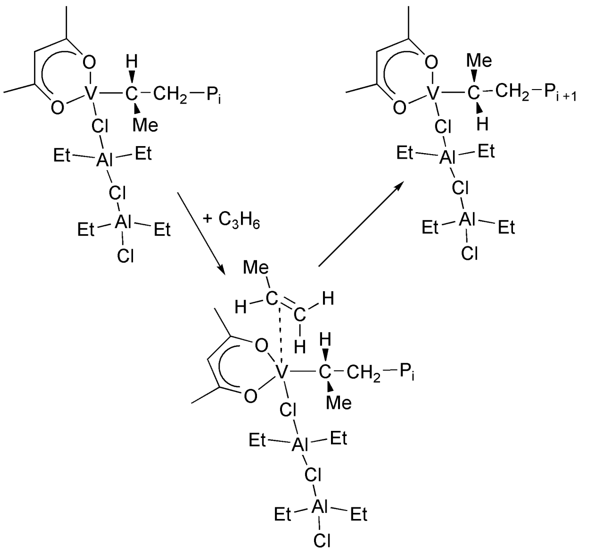


Fig. 4 Proposed structure and mechanism for the chain propagation in the living polymerization of propene with the soluble $V(acac)_3/Et_2AlCl$ system.

The presence of anisole during the copolymerization was essential, otherwise non-negligible amounts of homopolymers with lower molecular weights were formed. Alternatively, transformation of the living polypropene ends into cationic polymer ends by reaction with molecular iodine followed by treatment with $AgClO_4$ in THF resulted in the ongoing living polymerization of THF to give a propene–tetrahydrofuran diblock-copolymer (see Fig. 5).

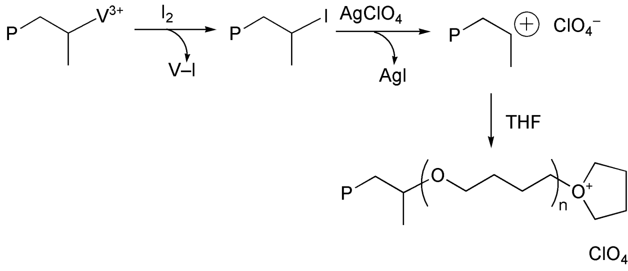


Fig. 5 Synthesis of a propene–tetrahydrofuran diblock copolymer.

4 Other monomers

In addition to the broad application of vanadium-based catalysts in the (co)polymerization of ethene and propene, they have also been used to polymerize other monomers. These monomers are most often used in co-polymerization with either ethene or propene, but some examples of homo-polymerization are known as well. When $VO(OEt)_3$ was used in the homopolymerization of isoprene with an organoaluminium compound as co-catalyst, the results depended very much on the nature of the co-catalyst.[13] In the case of Et_2AlCl, isoprene was oligomerized to a mixture of dimers, trimers and higher oligomers. Changing the aluminium compound to either Et_3Al or $EtAlCl_2$ resulted in the formation of polymeric material only. With Et_3Al isoprene was polymerized to a liquid polymer, whereas with $EtAlCl_2$ an insoluble polymer was obtained.

A large variety of monomers has been used in the co-polymerization with either ethene or propene or in the ter-polymerization with both ethene and propene.[14] These monomers include α-olefins, internal olefins, conjugated or non-conjugated dienes and cyclic olefins. As an example, butadiene and propene could be polymerized to an alternating butadiene–propene co-polymer.[15] The catalytic system consisted of $VO(OCH_2CMe_3)_2Cl/(i\text{-}Bu)_3Al$ and the reaction had to be carried out at low temperature (< -10 °C). In this way almost perfectly alternating co-polymers were obtained with M_w values of more than 70 kg mol^{-1}. A mechanism for this reaction was proposed by Shuke and Dingshing.[16] They proposed the catalytically active species to be an aluminium/vanadium dimer with the vanadium nucleus in the 3+ oxidation state (Fig. 6). Reaction of butadiene with this species gives a π-allyl complex. As only one vacancy is left, only propene can react. Insertion of the propene forms a transition state with two vacancies, which is stabilized by butadiene. Formation of a π-allyl complex again and repetition of the sequence creates an alternating co-polymer.

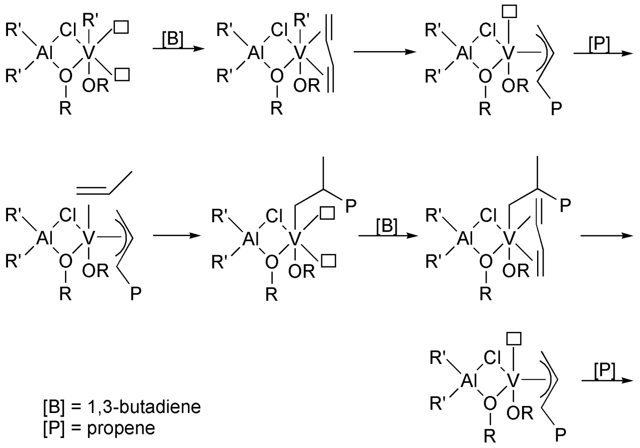


Fig. 6 Postulated mechanism for alternating copolymerization of butadiene [B] and propene [P].

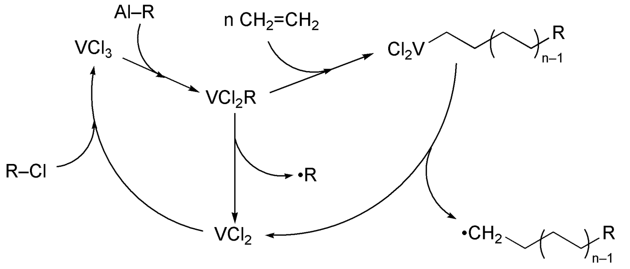
Polymerization of various polar monomers, such as halogen-, amine-, and ester-containing compounds, has been reported as well. The use of polar co-monomers has been the subject of a recent review by Boffa and Novak.[17]

5 Promoters

As stated before, one of the main disadvantages of vanadium-based polymerization catalysis is the fast deactivation associated with the reduction to inactive vanadium(ɪɪ) species. This reduction causes systems with very high initial activities to have very poor overall productivities. One way to overcome this problem is the reactivation of inactive vanadium(ɪɪ) centres to active vanadium(ɪɪɪ) species by addition of so-called 'rejuvenators' or 'promoters'. Several examples of such compounds are known in the literature but halogenated hydrocarbons have been used most often and will be discussed here.

Already in the late 1960s it was recognized that halogenated hydrocarbons could be used to boost the activity of vanadium-based catalysts. Hexachlorocyclopentadiene (HCP) was used in combination with several vanadium catalyst precursors by Gumboldt *et al.*[18] They found that the vanadium(ɪɪ) species obtained by reduction with aluminium alkyls were inactive in ethene polymerization, but became active after addition of HCP.

Christman investigated these effects in the homogeneous polymerization of ethene.[19] In order to maintain a true homogeneous system the temperature had to be higher than 105 °C. At these temperatures deactivation is very rapid, but continuous addition of an aluminium alkyl and a polyhalogenated hydrocarbon promoter assured that the polymerization reaction proceeded. All polyhalo-promoters cause an increase in polymerization activity but their efficiencies vary considerably. Esters of trichloroacetic acid appeared to be the preferred promoters. To check the effect of methyl trichloroacetate (MTCA) on the oxidation state of the vanadium, the precatalyst $VO(O\text{-}t\text{-}Bu)_3$ was first reduced by Et_2AlCl to a mixture of either V^{4+} and V^{3+} or V^{3+} and V^{2+}, depending on the Al : V ratio. Addition of MTCA caused the overall oxidation state to increase, indicating that MTCA is capable of oxidizing both V^{2+} and V^{3+}. Based on these findings, the reaction pathway shown in Scheme 1 was proposed.



Scheme 1 Simplified reaction pathway for the ethene polymerization with vanadium catalysts and halogenated hydrocarbons.

It should be noted that all vanadium species in this scheme are undoubtedly complexed with the various aluminium species present. In fact, uncomplexed VCl_2 and VCl_3 are insoluble. Another way of improving catalytic performance is the use of an organotin hydride in combination with a halogenated hydrocarbon. In the ter-polymerization of ethene/propene/diene relative productivity increments of 1.3 to 1.7 were observed depending on both the vanadium catalyst and the halocarbon used.[5] Tributyltin hydride (TBTH) was the most effective, although dibutyltin dihydride also showed an increase in activity.

The effect of TBTH appears to be based on an enhancement of the re-oxidation of the vanadium catalyst by the chlorinated activator, which results in an increase of the average number of active species.

The use of halocarbons as activators is not only limited to 'low temperature' homogeneous catalysis, but they can also be employed in heterogeneous catalysis at high temperatures (160 °C).[20] However, halocarbon esters behave more as deactivators at high temperatures because under those conditions they react with aluminium alkyls to give inactive aluminium alkoxides.

6 Ligand-controlled catalysis

Several ligand systems have been applied in vanadium chemistry to improve catalytic activity or to gain control over the polymer formed. Here they will be discussed according to the oxidation state of the vanadium nucleus.

6.1 Vanadium(v)

One of the problems associated with the use of vanadium(v) complexes as catalysts for Ziegler–Natta polymerizations is that hydrocarbyl compounds of vanadium(v) are easily reduced to lower-valent complexes. Gibson *et al.* reported the use of $[CpV(=N\text{-}p\text{-}Tol)Cl_2]$ in ethene polymerization with either Et_2AlCl or MAO as co-catalyst.[21] With 1 bar ethene at room temperature relatively low activities were found (15 and 27 kg PE per mol[V]·h). They do not give the oxidation state of the catalyst, but the low activity is most probably due to bimolecular deactivation, since immobilising the catalyst by anchoring onto a polystyrene support resulted in a ten-fold activity increase. Murphy and Turner showed that steric protection of the vanadium nucleus by the bulky 2,6-diisopropylimido ligand allows the synthesis of benzylvanadium(v) complexes.[3] However, this stability might be specific for the benzyl group since Chan *et al.* showed that treatment of [CpV(=NC_6H_3(*i*-Pr)$_2$-2,6)Cl_2] with MeMgBr or $AlMe_3$ resulted in reduction to vanadium(IV) species.[22] Scheuer *et al.* used the hydrotris(pyrazolyl)borato ligand (Tp*) in combination with imido ligands for the synthesis of vanadium(V) catalysts.[23] [Tp*V(=NC_6H_3(*i*-Pr)$_2$-2,6)Cl_2] catalyzed the polymerization of ethene at atmospheric pressure and of propene at 7 bar with MAO as co-catalyst. However, activities and molecular weights were low (14 kg PE per mol[V]·h, M_w = 47000; 1 kg per PP mol[V]·h·bar, M_w = 3800). The oxidation state of the actual catalyst is unknown.

Feher *et al.* reported on the use of vanadium-containing silsesquioxanes (Fig. 7) as catalyst.[24]

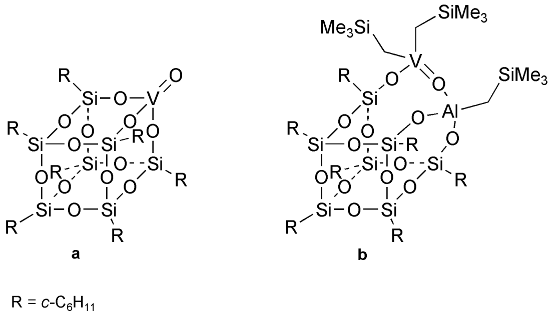


Fig. 7 Vanadium containing silsesquioxanes used by Feher *et al.*

Compound 7**a** catalysed the polymerization of ethene at room temperature and 1 bar of ethene pressure to low molecular weight polyethene (M_n = 21000, M_w = 47900) with $AlMe_3$ as the co-catalyst. The presence of the silsesquioxane backbone is crucial, since neither $(Ph_3SiO)_3VO$ nor (*n*-PrO)$_3$VO gave polyethene under the same conditions. This system is also capable of polymerizing propene and 1,3-butadiene. Whereas the activity for propene was very low, butadiene was completely polymerized to >95% *trans*-1,4-polybutadiene within 30 minutes. The narrow polydispersity of 2.28 in the case of ethene polymerization indicates that a well-defined catalyst is formed under reaction conditions. On reaction of **7a** with $(Me_3SiCH_2)_3Al$ such a catalyst species **7b** was isolated and characterized.

6.2 Vanadium(IV)

Only a few examples of vanadium catalysts in the 4+ oxidation state are known. Motevalli *et al.* reported the preparation of a vanadium(IV) oxocyclosiloxane [VO{O$(SiPh_2O)_2$}$_2$-μ-(Li-$(THF)_2$]$_2$ (Fig. 8) by reacting VCl_4 with three equivalents of

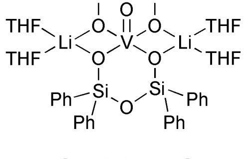


Fig. 8 (Cyclosiloxy)oxovanadium(IV) complex used by Motevalli *et al.*

[O$(SiPh_2OLi)_2$·$(THF)_2$].[25] It was tested in the polymerization of both ethene and propene with 10 equivalents of $AlMe_3$ as co-catalyst. At 20 °C and 35 bar ethene pressure very high molecular weight polyethene was obtained in 30 seconds with an activity of 110 kg PE per mol[V]·h. The molecular weight could not be determined due to the insolubility of the material. The activity in propene polymerization was very low and only oligomers were formed. The catalytically active species probably contains vanadium(IV). After removal of the excess $AlMe_3$ a compound was isolated which was active in ethene polymerization without addition of extra $AlMe_3$. EPR analysis of this compound showed the characteristic eight-line pattern of vanadium(IV).

Gambarotta and co-workers reported the use of organic amides as ancillary ligands for the synthesis of tetravalent amidovanadium halides $(R_2N)_2VCl_2$ (R = *i*-Pr, *c*-C_6H_{11}).[26] These dichloro species were alkylated by treatment with alkyllithium reagents to give $(R_2N)_2VR'_2$ (R′ = Np, Ph, Bz). The latter compounds did not show any significant polymerization activity under the usual reaction conditions except for butadiene. Treatment with Lewis acids like VCl_3 or $B(C_6F_5)_3$ gave no improvement. However, addition of $AlCl_3$ resulted in the formation of an active catalyst, which again shows that the presence of both aluminium and vanadium is necessary to produce catalytic activity. The dichloro compounds $(R_2N)_2VCl_2$ were tested in ethene polymerization at 20 °C and 1 bar ethene pressure with a wide variety of co-catalysts (Me_3Al, Et_3Al, $EtAlCl_2$, $Et_{1.5}AlCl_{1.5}$, *i*-$BuAlCl_2$). The best combination had an activity of 256 kg per mol[V]·h. The activity profile was such that during the first 15–30 minutes production of polyethene was high, after which the reaction proceeded at a low steady state for about 20 h and then stopped. Addition of chlorinated hydrocarbons (BzCl, $ClCH_2CH_2Cl$ or $CHCl_3$) followed by co-catalyst restarted the polymerization. The dichloro compounds were also tested in ethene/propene copolymerization with a series of $R_xAlCl_{(3-x)}$ co-catalysts under 2 bar pressure. The activity with Et_3Al was low but increased with increasing chlorine content of the co-catalyst and reached a maximum for $Et_{1.5}AlCl_{1.5}$ (860 kg EP per mol[V]·h). The polymer contained approximately 28 wt% propene and the molecular weight was high (M_w = 2293000, M_w/M_n = 3.0).

Choukroun and co-workers used a chelated diamidovanadium(IV) catalyst (Fig. 9).[27a] The ligand, [$Me_2C(CH_2N(Si$-*t*-$BuPh_2))_2$]$^{2-}$, contains sterically demanding protecting silyl groups, which should lower the electron density on the metal centre. The complex was tested in ethene polymerization (20 °C, 1 atm) with MAO as co-catalyst (Al/V 500:1) in toluene and only low activity was observed. Changing the solvent to pentane resulted in a slight increase in activity. This difference was attributed to deactivation by coordination of toluene to the cationic centre. The low activity of this complex (and those of corresponding group IV complexes) was attributed to screening of the catalytic centre by the bulky silyl groups. Alternatively, the N–Si bond could have been cleaved by the excess MAO, as the authors had observed earlier for vanadium complexes.

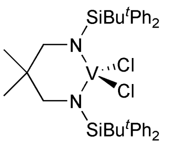


Fig. 9 Chelating diamido vanadium(IV) catalyst used by Choukroun *et al.*

The same authors also reported two vanadium(IV) arylimido complexes as catalysts (Fig. 10).[27b] These complexes displayed high activities of 220 and 1200 kg PE per mol[V]·h·atm, respectively, after activation with $EtAlCl_2$. When complex **b** was used in combination with MAO a much lower activity was found.

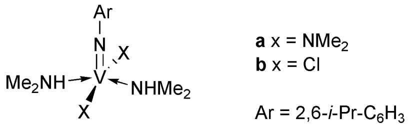


Fig. 10 Vanadium(IV) imido complexes used by Choukroun *et al.*

Witte *et al.* synthesized a so-called ‘constrained geometry’ catalyst based on vanadium(IV) (Fig. 11) and compared its activity in ethene polymerization with MAO as co-catalyst to

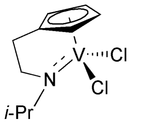


Fig. 11 'Constrained geometry' catalysts used by Witte *et al.*

that of its Ti(IV) congener.[28] Under identical conditions, the activity of the vanadium catalyst was noticeably lower than that of the titanium catalyst. Also the molecular weight of the polymers was much lower for vanadium (M_w = 14900, M_n = 4900, M_w/M_n = 3.0) than for titanium (M_w = 139000, M_n = 59500, M_w/M_n = 2.3). ^{1}H NMR analysis of the polymer endgroups showed that β-H transfer is the dominant chain-transfer route for the vanadium-based catalyst.

6.3 Vanadium(III)

Sobota and co-workers used chelating oxygen-based ligand systems to synthesize vanadium(III) complexes.[29] Treatment of VCl_3 with ethyl acetate gave $[V_2(\mu\text{-}Cl)_2Cl_4(MeCO_2Et)_4]$, which was converted to $[V_2(\mu\text{-}Cl)_2Cl_4\{CH_2(CO_2Et)_2\}_2]$ by substitution with ethyl malonate. Both complexes were tested in ethene polymerization. Comparison with $[VCl_3(THF)_3]$ and $[V_2(\mu\text{-}Cl)_2Cl_4(THF)_4]$ showed that the activities are comparable, which is not surprising since all four compounds are oxygen-based Lewis base adducts of vanadium trichloride. They also used the bulky phenoxide ligand $[OC_6H_3\text{-}(i\text{-}Pr)_2\text{-}2,6]^-$, (Fig. 12). The complexes **a**,**b** and **d** were tested in ethene polymerization (6 bar, 50 °C, hexene, 500 equiv. Et_2AlCl) using $MgCl_2$ to prevent reactor-fouling. For complex **a** a high activity of 9400 kg PE per mol[V]•h was found, which was increased to 12400 kg PE per [mol]V•h by raising the temperature to 70 °C. With MAO as the co-catalyst (Al/V 1000:1) a much lower activity (1680 and 4990 kg PE per [mol]V•h, respectively) was observed. The complexes **b** and **d** displayed only low activities.

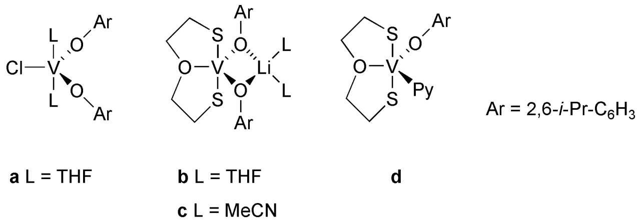


Fig. 12 Vanadium(III) phenolate complexes used by Sobota and co-workers.

Recently Gambarotta and co-workers reported the effects of ligand modification on the polymerization behaviour of (β-diketonate)$_3$V complexes.[30] They used different ligands to study the solubility (Cy-acac), steric effects (*t*-Bu-acac) and the combination of steric and electronic effects (F-acac) (Fig. 13).

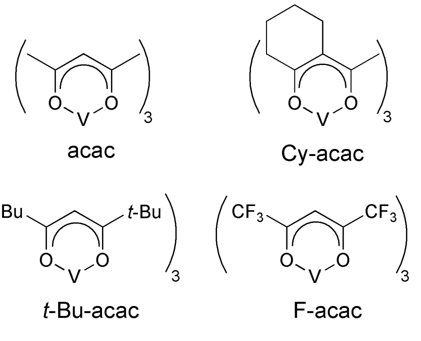


Fig. 13 Vanadium-acac complexes used by Gambarotta and co-workers.

The four vanadium catalysts were tested in ethene/propene copolymerization at 22 °C and 2 bar total pressure with either Et_2AlCl or $Et_{1.5}AlCl_{1.5}$. It turned out that both the structure of the ligand system and the chlorine content of the co-catalyst had little influence on catalytic activity. The incorporation of propene in the EP elastomer was lower in case of *t*-Bu-acac and F-acac, but the difference was small. These results show that the catalytic site is very open and probably far removed from the β-diketonate ligand. The primary role of the aluminium co-catalyst is thus abstraction of at least two if not all three acac ligands from the vanadium centre.

Completely different results are obtained when the nitrogen analogues of β-diketonates, β-diiminates, are used.[31a] Budzelaar *et al.* reported on vanadium(III) mono(β-diiminato) complexes, $LVCl_2$ (Fig. 14, **a** and **b**), which may be alkylated to give remarkably stable LVR_2 complexes (R = Me, *n*-Bu). Treatment of the complexes with either MAO or Et_2AlCl resulted in transfer of the β-diiminato ligand to aluminium and no significant polymerization activity was observed. The steric bulk of the substituent on the nitrogen atoms is probably the explanation for these observations, as changing them to phenyl groups (Fig. 14, **c**) resulted in completely different findings. Kim *et al.* prepared the dichloride $L(\mathbf{c})VCl_2(THF)_2$ and tested it in ethene polymerization with MAO (130 equiv.) as co-catalyst.[31b] High molecular weight (M_w = 2.0 × 10^6, M_n = 1.1 × 10^6) polyethene with a narrow molecular weight distribution (M_w/M_n = 1.75) was obtained. The compound also showed activity in ethene/propene copolymerization. ^{2}H NMR analysis of a mixture of $LVCl_2(THF)_2$ (L contained deuterated phenyl groups) with excess MAO indicated that the ligand remained on the vanadium centre and no transfer to aluminium occurred.

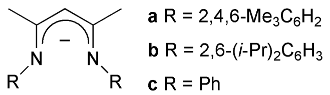


Fig. 14 β-Diiminato ligands used by Budzelaar *et al.* (**a**,**b**) and Kim *et al.* (**c**).

A second class of monoanionic N,N-chelating ligands are the amidinates which have been introduced by Teuben and co-workers (Fig. 15).[32] Both ligands **a** and **b** were used to synthesize mono- and dichloro vanadium(III) compounds, $LVCl_2(THF)_2$ and L_2VCl. The monochlorides could be alkylated to yield $L(\mathbf{a})_2VR$ (R = Me, Et, allyl) and $L(\mathbf{b})_2VR$ (R = Me, allyl). Alkylation of the dichloride was only possible in the case of ligand **b** with R = allyl. Complex $L(\mathbf{a})_2VMe$ turned out to be a well-defined catalyst. It oligomerized ethene at 80 °C in C_6D_6 to yield a Flory–Schultz distribution of linear 1- and 2-alkenes. Although the catalysis was slow, all vanadium centres appeared to be involved. The low activity was attributed to the relatively low electrophilicity of the metal centre. In order to improve the activity, ligand **a** was modified with an electron-withdrawing substituent, $[C_6F_5]^-$ to give ligand **c**. When exposed to ethene (8 bar, 80 °C, toluene) $L(\mathbf{c})_2VMe$ produced polymeric material (M_n = 1780, M_n/M_w = 2.3) with an activity of 8.1 kg per mol[V]•h, which was more than five times higher

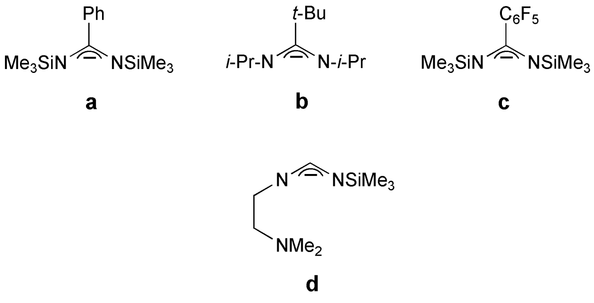
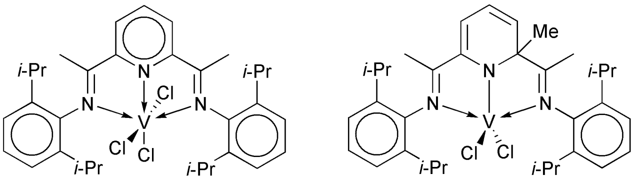


Fig. 15 Amidinate ligands used by Teuben and co-workers.

than the productivity of L(**a**)$_2$VMe. The tridentate ligand **d** was used to synthesize the vanadium(III) dichloro compound L(**d**)VCl$_2$(THF). It was tested in ethene polymerization (10 μmol, 250 ml toluene, 6 bar ethene) with 20 equivalents of Et$_2$AlCl as co-catalyst. It was most active at 30 °C (447 kg per mol[V]·h·bar) and the molecular weight distribution of the product was characteristic for the presence of a single active site. Increasing the temperature resulted in a drastic drop in activity and at 80 °C catalyst decomposition was rapid. Comparison with the results found for L(**a**)VCl$_2$(THF)$_2$ under similar conditions showed that the pendant NMe$_2$ group improved the polymerization activity, but that it did not improve the thermal stability of the active species.

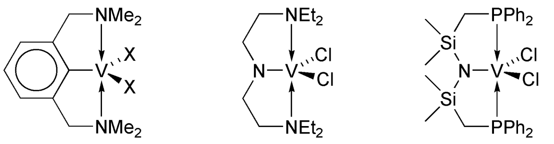
A third class of nitrogen-based ligands is formed by the neutral diimine/pyridine derivatives recently used by Gibson and Brookhart in iron-based Ziegler–Natta catalysis.[33] Gambarotta and co-workers have extended the use of these ligands to vanadium chemistry and treatment of [VCl$_3$(THF)$_3$] with 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine gave the corresponding coordination product (Fig. 16 **a**).[34a] Treatment of **a** with MAO resulted in methylation of the *ortho* position of the pyridine ring and removal of one of the chlorine atoms (Fig. 16 **b**). In this process the ligand is transformed into an anionic amide. Both complexes polymerized ethene with similar activities with MAO as the co-catalyst and produced polymers with similar characteristics. Vanadium(III) complexes of **a** and the α-diimine ligands [PhN=C(Me)–C(Me)=Ph] and [{2,6-(i-Pr)$_2$Ph]N=CH–CH=N[iPr)$_2$Ph}] were used by Grassi *et al.* as ethylene polymerization catalysts together with AlEt$_2$Cl and MAO.[34b]



a **b**

Fig. 16 Vanadium complexes used by Gambarotta and co-workers.

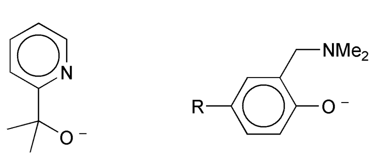
In an Exxon patent the use of monoanionic tridentate aryl and amido ligands has been claimed (Fig. 17).[35] The compounds **a**, **c** and **d** were tested with MAO as the co-catalyst in both ethene homopolymerization as well as ethene/hexene copolymerization The highest activity in ethene polymerization was found for compound **c**. At 60 °C it was 2145 kg per mol[V]·h. The polymer had a molecular weight of 1.1 × 10^6 g per mol and a molecular weight distribution (M_w/M_n) of 2.5. The activity of all three compounds was considerably less in the hexene co-polymerization. The methylated compound **b** was used in ethene and propene homo-polymerizations as well as in ethene/hexene co-polymerization with [CPh$_3$][B(C$_6$F$_5$)$_4$] as the activator. The activity in ethene polymerization was highest at 115 °C (100 kg per mol[V]·h). Again the activity dropped in the polymerization of higher olefins.



a X = Cl
b X = Me
c
d

Fig. 17 Monoanionic tridentate aryl and amido ligands.

In our group, we have recently investigated the use of O,N-chelating ligands in vanadium-based systems (Fig. 18).[36]



a **b** R = H, Me, *t*-Bu, Cl, N=NPh, MeO

Fig. 18 O,N-chelating ligands used by Hagen *et al.*

Ligand **a** was used in vanadium(V) chemistry resulting in the synthesis of the complexes [VOCl$_2$(OCMe$_2$[2-Py])] and [V(=N-*p*-Tol)Cl$_2$(OCMe$_2$[2-Py])]. These compounds were tested in ethene polymerization together with several other non-chelated vanadium(V) oxo and imido compounds. Whereas [VOCl$_2$(OCMe$_2$[2-Py])] displayed a reasonable activity (88 kg PE per mol[V]·h·bar at 50 °C), [V(=N-*p*-Tol)Cl$_2$(OCMe$_2$[2-Py])] showed almost no activity under similar circumstances and for both complexes the activities were much lower than those of the non-chelated counterparts. We tentatively assign this decrease in activity to a smaller number of catalytically active species.

The *o*-aminophenolate ligands **b** were used in both vanadium(III) and (IV) chemistry. Whereas a well-defined vanadium(III) chloro complex, [VCl(OC$_6$H$_3$(CH$_2$NMe$_2$)-2-Me-4)$_2$] was prepared, for the vanadium(IV) compounds, only unidentified complexes were obtained in the reaction of VOL$_2$ with SOCl$_2$. Nevertheless, since their elemental composition was known, they were tested as well. The complexes were used as catalysts in the co-polymerization of ethene and propene. The activities varied between 21 and 222 kg mol[V]·h·bar. The large difference in activity was attributed to differences in solubility. IR-analysis of the polymers shows that the incorporation of propene varied between approximately 30 and 40%. The molecular weights of the polymers, based on their intrinsic viscosities (in decalin at 135 °C), varied between 5.0 × 10^5 and 10.5 × 10^5 g per mol. The results were too preliminary to draw solid conclusions about the influence of either valence state or ligand.

7 Summary remarks

In the present review we have tried to demonstrate that over the years extensive searches have been made for homogeneous vanadium catalysts for the polymerisation of α-olefins. This has lead to the synthesis of fascinating complexes with a wide variety of ligands and various oxidation states of the vanadium centre. Although the structures of many of these complexes have been thoroughly characterized by *e.g.* X-ray crystallography, and the catalysts are therefore theoretically well-defined, still very little is known about the actual catalytically active species. Under the influence of the co-catalyst, many changes can occur such as change of oxidation state, removal of ligands, *etc.* Moreover, in most cases the number of active centres is just a fraction of the total amount of catalyst. All this makes it difficult, if not impossible, to pinpoint the active species. Of course, knowledge of its structure is not a prerequisite for a good catalyst, but it would make designing one a more exact science.

With respect to what is a good catalyst, this is actually difficult to say (and it, of course, depends on what one wants, *i.e.*, high activity, high incorporation of co-monomer *etc.*). Activity numbers are often not comparable, because the conditions are completely different and are sometimes not given at all.

8 Acknowledgements

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