[Regular Paper]

Effect of Al Cocatalyst in Ethylene and Ethylene/Norbornene (Co)polymerization by (Imido)vanadium Dichloride Complexes Containing Anionic N-Heterocyclic Carbenes Having Weakly Coordinating Borate Moiety

Go Nagai 1†, Takato Mitsudome 1†2*, Ken Tsutsumi 1†, Shunsuke Sueki 1†, Toshiaki Ina 1†3, Matthias Tamm 4†4*, and Kotohiro Nomura 1†1*

† 1) Dept. of Chemistry, Tokyo Metropolitan University, 1-1 Minami Osawa, Hachioji, Tokyo 192-0397, JAPAN
† 2) Dept. of Materials Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, JAPAN
† 3) Japan Synchrotron Radiation Research Institute (JASRI, SPring-8), Sayo, Hyogo 679-5198, JAPAN
† 4) Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30, 38106 Braunschweig, GERMANY

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Effect of Al cocatalyst in ethylene polymerization using (imido)vanadium(V) complexes containing anionic N-heterocyclic carbenes with a weakly coordinating borate moiety in 4-position (WCA-NHC), [V(N-2,6-Me2C6H3)Cl2(WCA-NHC)] [1; NHC = 1,3-bis(2,6-dimethylphenyl)-imidazolin-2-ylidene], have been explored. The activities by I upon presence of AlBu3 in ethylene polymerization and in the copolymerization with norbornene (NBE) were higher than those in the presence of MAO, and the resultant poly(ethylene-co-NBE)s prepared by 1-AlBu3 catalyst possessed uniform molecular weight distributions and compositions. Formation of vanadium(III) species could be assumed upon presence of AlBu3, especially on the basis of both NMR and ESR spectra (silent) and certain significant changes in the V K-edge XANES (pre-edge and edge region) spectrum, whereas no significant changes in the XANES spectrum were observed from the toluene solution containing I upon addition of MAO. It is thus suggested that a difference in the catalyst performances between in the presence of MAO and AlBu3 should be due to a formation of different catalytically active species with different oxidation states.

Keywords
Ethylene polymerization, Vanadium complex catalyst, Aluminum cocatalyst, Oxidation state, Norbornene, XANES

1. Introduction

Metal catalyzed olefin polymerization is an important key reaction especially in polyolefin industry, and design and development of efficient molecular catalysts that precisely control olefin insertion/propagation have been one of the most attractive subjects1)−15). Due to a unique characteristics of high reactivity toward olefins displayed in the polymerization using the classical Ziegler-type vanadium catalyst systems [e.g. consisting of V(acac)3, VOCl3 etc. and Et2AlCl, EtAlCl2, 2BuLi etc.]16)−18), design and synthesis of the efficient vanadium complex catalysts attract considerable attention19)−21). (Imido)vanadium(V) complexes containing anionic donor ligands (X) of the type, V(NAr)Cl2(X) (X = arylxoo, imidazolin-2-2imino etc.)19), are known to exhibit remarkable activities for the ethylene polymerization19)−25) and the copolymerization with norbornene (NBE)20)−23),24). We recently reported that the (imido)vanadium(V) complexes containing anionic N-heterocyclic carbenes with a weakly coordinating borate [B(C6F5)3] moiety (WCA-NHC)25)−31) of the type, V(NR)Cl2(WCA-NHC) [R = 1-adamantyl, C6H5, 2,6-Me2C6H3; NHC = 1,3-bis(2,6-dimethylphenyl)-imidazolin-2-ylidene], especially V(N-2,6-Me2C6H3)Cl2(WCA-NHC) (I) exhibited remarkable catalytic activity for ethylene polymerization in the presence of AlBu325), which has been commonly considered as an ineffective Al cocatalyst in the polymerization not only using ordinary metallocones1)−4), half-titanocones5)−7), and the others8)−10), but also using the other (imido)vanadium(V) dichloride complexes with anionic ancillary donor ligands10)19)−24). The activity in the ethylene polymerization by 1-AlBu3 catalyst was apparently higher than those by I in the presence of methylaluminoxane (MAO), Et2AlCl co-

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* To whom correspondence should be addressed.
E-mail: mitsudome@cheng.es.osaka-u.ac.jp, m.tamm@tu-bs.de or ktnomura@tmu.ac.jp

Therefore, in this paper, we explored the copolymerization with NBE using 1 to confirm the effect of Al cocatalyst toward both the activity and copolymerization behavior (Scheme 1). Moreover, we explored analysis of the catalyst solution by $^{51}$V nuclear magnetic resonance (NMR) and electron spin spin resonance (ESR) spectra, and V K-edge X-ray absorption near edge structure (XANES) spectra. Through this study, we wish to demonstrate that the observed different catalyst performances between in the presence of MAO and Al$^3$Bu$_3$ should be due to a formation of different catalytically active species with different oxidation states.

2. Results and Discussion

2.1. Ethylene Copolymerization with Norbornene (NBE) Using V(N-2,6-Me$_2$C$_6$H$_3$)Cl$_2$(WCA-NHC) (1)-Al Cocatalyst Systems

V(NAr)Cl$_2$(WCA-NHC) (1, Ar = 2,6-Me$_2$C$_6$H$_3$) has been chosen in this study, because, as described above, 1 showed the highest activity for ethylene polymerization using V(NR)Cl$_2$(WCA-NHC) [R = 1-adamantyl (Ad), C$_6$H$_5$ (Ph), Ar (I)] in the presence of Al cocatalysts$^{25}$). Table 1 summarizes the results in the copolymerization of ethylene with norbornene (NBE) in the presence of MAO or Al$^3$Bu$_3$. The results for ethylene polymerization$^{25}$) were also placed for comparison.

It turned out that 1 showed high catalytic activities for the ethylene/NBE copolymerization in the presence of Al$^3$Bu$_3$ (runs 6-10), which is known to be ineffective cocatalyst in olefin polymerization by ordinary transition metal complex catalysts$^{1}$,2$^{10}$,2$^{21}$, as described in the introductory. It also turned out that the activity was affected by the Al/V molar ratio and the initial NBE concentration, although the optimized Al/V molar ratios exhibiting the high activity in the copolymerization (runs 4-6, 8, 9) were somewhat different from that in the ethylene homo polymerization (runs 1-3)$^{25}$. Moreover, the $M_n$ values in the resultant polymers decreased upon increasing the NBE concentration. As observed in the ethylene homo polymerization$^{25}$, the activities in the copolymerization in the presence of MAO cocatalyst were lower than those in the presence of Al$^3$Bu$_3$. Notable differences in the activities (calculated on the basis of polymer yields) in the copolymerization upon addition of NBE were not observed compared to those

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<th>Cocat.</th>
<th>Al/V</th>
<th>NBE$^c$</th>
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<th>Yield</th>
<th>Activity$^d$</th>
<th>$M_n$</th>
<th>$M_w$/$M_n$</th>
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a) Conditions: toluene 30 mL, ethylene 8 atm, 25°C.
b) Molar ratio of Al/V.
c) Initial NBE concentration in mmol/mL.
d) Activity in kg-polymer/mol V h.
e) GPC data in o-dichlorobenzene vs. polystyrene standards.
f) Cited from reference 25. 

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in the ethylene polymerization in these catalyses.

The resultant polymer prepared by 1-Al\textsubscript{i}Bu\textsubscript{3} catalyst under certain conditions (run 10) possessed rather high molecular weight with low PDI (\(M_w/M_n\)) value with uniform distribution; the uniform composition in the copolymer was confirmed by DSC thermogram\textsuperscript{32). Figure 1 shows the \(\textsuperscript{13}C\) NMR spectrum in the copolymer (sample run 10, in 1,1,2,2-tetrachloroethane-\(d_2\) at 110 \(^\circ\)C) of Poly(ethylene-co-NBE) Prepared by 1-Al\textsubscript{i}Bu\textsubscript{3} Catalyst (sample run 10, NBE content 21.4 mol%).

Most of all resonances could be assigned and the resultant polymer possessed microstructures corresponding to the isolated and the alternating NBE incorporations (a mixture of \textit{iso} and \textit{syndio} stereo regularity)\textsuperscript{20),21),33)\btextsuperscript{35). It should be noted that the NBE content in the resultant copolymer (21.4 mol%) was higher than those prepared by the reported (imido) vanadium(V) dichloride complexes containing aryloxo ligands, exemplified as V(NAr)Cl\textsubscript{2}(O-2,6-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{3}), under the similar conditions [15.9 mol\% (MAO co-catalyst, NBE 0.30 M), or 17.9 mol\% (Et\textsubscript{2}AlCl co-catalyst, NBE 0.50 M)]\textsuperscript{20). Although the \(M_n\) values in the resultant copolymers were rather low, an improvement in the NBE incorporation was thus observed in this catalysis\textsuperscript{36).}

2. 2. Analysis of Catalyst Solution Consisting of V(N-2,6-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{3})Cl\textsubscript{2}(WCA-NHC) (1) and Al\textsubscript{i}Bu\textsubscript{3} Cocatalysts in Toluene by NMR, ESR, and Solution-phase X-ray Absorption Spectroscopy

Figure 2 shows \(^{51}\text{V}\) NMR spectra of toluene-\(d_8\) solution containing the dichloride complex (1) in the presence of 10.0 equiv of MAO, Al\textsubscript{i}Bu\textsubscript{3} (at 25 \(^\circ\)C). A resonance ascribed to 1 at 303 ppm (Fig. 2 a)) was disappeared upon addition of Al\textsubscript{i}Bu\textsubscript{3} (10.0 equiv, Fig. 2 b)), whereas a decrease in the intensity was observed upon addition of MAO (10.0 equiv, Fig. 2 c)). Since the disappearance of resonance upon addition of Al\textsubscript{i}Bu\textsubscript{3} suggests a possibility of generating certain paramagnetic species, ESR spectra of the similar toluene solutions were thus measured (Fig. 3)\textsuperscript{37),39,40). No significant differences in the spectrum were observed when a toluene solution containing 1 was added MAO (10.0 equiv, Fig. 3 b)). Moreover, the observed resonances were weak when a toluene solution containing 1 was added Al\textsubscript{i}Bu\textsubscript{3} (10.0 equiv, Fig. 3 c)). These ESR spectra clearly suggest that possibilities of formation of paramagnetic species, that would be observed in the ESR spectra [vanadium(IV) species], were negligible under these conditions (upon addition of MAO, Al\textsubscript{i}Bu\textsubscript{3}). Since the resonance corresponding to 1 was disappeared upon addition of Al\textsubscript{i}Bu\textsubscript{3} in the \(^{51}\text{V}\) NMR spectrum, formation of another species that could not be observed in both NMR and ESR spectra were thus highly assumed.

We thus focus on a possibility of synchrotron X-ray
absorption spectroscopy (XAS) for obtaining some information concerning the prepared catalyst solutions. In particular, the method (V-K edge analysis, 5.46 keV, through the use of synchrotron radiation at SPring-8, BL01B1 beamline) enables us to obtainment of information concerning structure and oxidation state by V-K pre-edge and edge peaks in XANES analysis. Figure 4 shows V K-edge XANES spectra of toluene solution containing 1 in the presence of MAO and Al\textsubscript{Bu}3 (10.0 equiv). The spectra of (imido)vanadium(V) trichloride, V(N-2,6-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{3})Cl\textsubscript{3}, and (imido)vanadium(IV) dichloride, V(NAd)Cl\textsubscript{2}(NMe\textsubscript{2}H)\textsubscript{2}, are also shown for comparison. The XANES spectrum of 1 shows pre-edge peak(s) at 5466.6 eV (5465.1 eV) and the spectrum of V(N-2,6-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{3})Cl\textsubscript{3} shows a similar pre-edge peak(s) at 5466.8 eV (5465.0 eV). Although the intensity of V(N-2,6-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{3})Cl\textsubscript{3} was rather low. The related (imido)vanadium(IV) dichloride, V(NAd)Cl\textsubscript{2}(NMe\textsubscript{2}H)\textsubscript{2}, showed a broad pre-edge peak at 5466.4 eV with low intensity compared to 1. Moreover, V(N-2,6-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{3})Cl\textsubscript{3} showed a shoulder-edge peak at 5477.6 eV, whereas 1 also showed a similar shoulder-edge peak at 5478.1 eV. V(NAd)Cl\textsubscript{2}(NMe\textsubscript{2}H)\textsubscript{2} also showed a similar shoulder-edge peak at 5477.5 eV. Two pre-edge peaks in 1 and V(N-2,6-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{3})Cl\textsubscript{3} are generally considered as due to a transition from 1s to 3d + 4p, although examples of solution V K-edge XANES spectra through use of the synchrotron radiation still have been limited. It turned out that certain difference in the XANES (edge region) spectrum was observed between (imido)vanadium(V) dichlorides [1, V(N-2,6-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{3})Cl\textsubscript{3}, and V(NAd)Cl\textsubscript{3}] and the (imido)vanadium(IV) dichloride [V(NAd)Cl\textsubscript{2}(NMe\textsubscript{2}H)\textsubscript{2}]. No significant differences in the XANES spectrum (pre-peak and edge) from that in 1 was observed upon addition of MAO, suggesting that the oxidation state of 1 was preserved upon addition of MAO. Although we only observed a decrease in the intensity of resonance ascribed to 1 upon addition of MAO in the V\textsuperscript{51} NMR spectrum (Fig. 2c), the result should also meet a good agreement with the ESR spectrum (no or negligible resonances) of the toluene solution (Fig. 3b). In contrast, it is noteworthy that certain significant changes in the XANES (pre-edge and edge region) spectrum were observed when 1 [5466.6 eV and 5465.1 eV (pre-edge), 5478.1 eV (shoulder-edge)] was treated with Al\textsubscript{Bu}3 [5465.7 eV (pre-edge), 5474.8 eV (shoulder-edge), Fig. 4]. Apparent decrease in the intensity of pre-edge peak upon addition of Al\textsubscript{Bu}3 clearly suggests certain structural changes by reacting with Al alkyls.

Taking also into account the facts that (i) no resonances were observed when 1 was treated with 10.0 equiv of Al\textsubscript{Bu}3 in toluene-d\textsubscript{8} at 25 °C, (ii) no resonance ascribed to a paramagnetic species of V(IV) were observed in the ESR measurement in the toluene solution, and (iii) the XANES (pre-edge and edge region) spectrum was different from the (imido)vanadium(IV) dichloride, it is thus assumed that certain vanadium(III) species by reduction were generated from 1 upon addition of Al\textsubscript{Bu}3. It is also suggested a formation of different active species with different oxidation states from the solution containing 1 upon addition of MAO and Al\textsubscript{Bu}3. This paper, we have shown that Al\textsubscript{Bu}3 is an effective Al cocatalyst in ethylene (co)polymerization using V(N-2,6-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{3})Cl\textsubscript{2}(WCA-NHC) (1), and the copolymerization with norbornene afforded the copolymer with uniform molecular weight distribution and composition. On the basis of NMR, ESR and V
K-edge XANES spectra of the catalyst solutions of 1 upon addition of Al(i-Bu)₃ or MAO, it is suggested that observed difference in the activities and the copolymerization behavior would be due to a formation of different catalytically active species with different oxidation states. As far as we know, this is the rare and clear demonstration to explain the observed difference by adopting approach using these spectroscopic methods, especially XAS. We believe that these approaches should be helpful to provide more clear information for the better understanding, explanation.

3. Experimental Section

3.1. General Procedure

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox. Anhydrous grade toluene (Kanto Chemical Co., Inc.) was transferred into a bottle containing molecular sieves (a mixture of 3Å 1/16, 4Å 1/8, and 13Å 1/16) in the drybox under nitrogen stream, and were passed through an alumina short column under N₂ stream prior to use. V(N-2,6-Me₂C₆H₃)Cl₂(WCA-NHC) (1) was prepared according to a published method[25]. Al(i-Bu)₃ was purchased from Kanto Chemical Co., Inc., and polymerization grade ethylene (purity > 99.9 %, Sumitomo Seika Chemicals Co., Ltd.) was used as received. Toluene and AlMe₃ in the commercially available methylaluminoxane [TMAO, 9.5 wt% (Al) toluene solution, Tosoh Finechem Corp.] were removed under reduced pressure (at ca. 50 °C for removing toluene, AlMe₃, and then heated at > 100 °C for 1 h for completion) in the drybox to give white solids[91,20,25].

All ¹³C and ⁵¹V NMR spectra were recorded on a Bruker AV500 spectrometer (125.77 MHz for ¹³C and 131.55 MHz for ⁵¹V). All spectra were obtained in the solvent indicated at 110 °C (for ¹³C) or 25 °C (for ⁵¹V) unless otherwise noted. Chemical shifts are given in ppm and are referenced to SiMe₄ (δ 0.00 ppm, ¹³C) and VOCl₃ (δ 0.00 ppm, ⁵¹V). Coupling constants and half-width values, Δν/2, are given in Hz.

3.2. Ethylene Copolymerization with NBE Using V(N-2,6-Me₂C₆H₃)Cl₂(WCA-NHC) (1)–Al Cocatalysts

Typical procedure is as follows. Ethylene copolymerizations were conducted in toluene by using a 100 mL scale autoclave, and a typical procedure (run 4, Table 1) is as follows. Toluene (29.5 mL), a prescribed amount of Al(i-Bu)₃, and NBE were charged into the autoclave in the drybox, and then the apparatus was placed under ethylene atmosphere (1 atm). After the addition of a toluene solution (0.5 mL) containing a prescribed amount of complex via a syringe, the reaction apparatus was pressurized to 7 atm (total 8 atm), and then the mixture was stirred magnetically for 10 min. After the above procedure, ethylene was purged, and the mixture was then poured into MeOH (150 mL) containing HCl (5 mL). The resultant polymer was collected on a filter paper by filtration and was adequately washed with MeOH and then dried in vacuo at 60 °C for 2 h.

3.3. ⁵¹V NMR Experiments in the Reaction of V(N-2,6-Me₂C₆H₃)Cl₂(WCA-NHC) (1) with Al Cocatalysts in Toluene-d₈

Typical procedure is as follows. Into a toluene-d₈ solution (ca. 0.6 mL) containing 1 (25 μmol, ca. 42 μmol/mL) placed in the freezer (−30 °C), Al cocatalyst (Al(i-Bu)₃ or MAO; 250 μmol, 10.0 equiv) was added. The mixture was then measured by ⁵¹V NMR spectrum at 25 °C within 10 min after the preparation.

3.4. ESR Measurements

ESR measurement was performed with a Bruker ER073 Spectrometer. A toluene solution containing V(N-2,6-Me₂C₆H₃)Cl₂(WCA-NHC) (1) and a toluene solution containing MAO (10.0 equiv) or Al(i-Bu)₃ (10.0 equiv) were mixed with their concentrations being kept at 2.5 μmol/mL for 1 and 25.0 μmol/mL for MAO or Al(i-Bu)₃. The tube was then placed into the instrument preset (ESR measurements were started in less than 10 min after the preparation). Experimental parameters: 9.4 GHz frequency, 0.10 mT modulation amplitude, power 1.0 mW for 1 + Al(i-Bu)₃ and 1 + MAO (0.6 mW for 1).

3.5. Analysis of Catalyst Solution by Solution-phase X-ray Absorption Spectroscopy

V K-Edge X-ray absorption fine structure (XAFS) measurements were carried out at the BL01B1 beam line at the SPring-8 facility of the Japan Synchrotron Radiation Research Institute (proposal nos. 2016A1455, 2016B1509). The measurements were conducted at room temperature (25 °C). A Si (111) two-crystal monochromator was used for the incident beam. V K-edge XAFS spectra of V complex samples (prepared as toluene solution, 50 μmol/mL) were recorded in the fluorescence mode using an ionization chamber as the I₀ detector and 19 solid state detectors as the I detector. The X-ray energy was calibrated using V₂O₅. Data analysis was performed with the REX2000 Ver. 2.5.9 software package (Rigaku Corp.). The XANES data was analyzed by removing the atomic absorption background using a cubic spline from the χ spectra and normalization of them to the edge height.

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References

32) However, the resultant polymer prepared by 1-MAO catalyst (run 15) possessed several (probably) glass transition temperatures with tiny trace of melting temperature of polyethylene, suggesting composition in the resultant polymer is not uniform.
34) Detailed analysis data were shown in the Supporting Information; Nomura, K., Tsunoda, M., Fujiki, M., Macromolecules, 36, 3797 (2003).
36) Copolymers of ethylene with cyclic olefins (exemplified in norbornene) has been known as the promising materials with high transparency, thermal resistance, low water absorption etc.
42) In ref. 37), Supporting Information, the XANES spectrum of V(NAO)C2 is good fitting of that on the basis of DFT calculation.
要 旨

ホウ素アニオン含有 N-ベテロ環状カルベン配位子を有するイミド配位バナジウム(V)錯体によるエチレン重合およびノルポルネンとの共重合における Al 助触媒の効果

永井 豪1), 潮留 敬人2), 堤 健1), 末木 俊輔1), 伊奈 秋哲3), Matthias TAMM4), 野村 琴広1)

1) 首都大学東京 理工学研究科，192-0397 東京都八王子市南大沢1-1
2) 大阪大学大学院基礎工学研究科物質創成専攻化学工学領域，560-8531 大阪府豊中市待兼山町1-3
3) (公財) 高輝度光科学研究センター，679-5198 兵庫県佐用郡佐用町光都1-1-1
4) Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30, 38106 Braunschweig, GERMANY

ホウ素アニオン含有 N-ベテロ環状カルベン（WCA-NHC）配位子を有するイミド配位バナジウム錯体、V(N-2,6-Me2C6H3)Cl2 (WCA-NHC) (1)，触媒によるエチレン重合およびノルポルネンとの共重合における触媒活性は、使用する Al 助触媒の影響を強く受け、特に AlBu3 助触媒存在下でメチルアルミニノキサン（MAO）より高活性を示した。触媒溶液の51V NMR スペクトル測定および ESR 測定、V K-Edge XANES 測定より、MAO の存在下での触媒溶液では倍数变化が見られないのに対し、AlBu3 の存在下の触媒溶液では NMR および ESR スペクトルが観察されず、XANES スペクトルより Al による還元反応が進行している可能性が示唆された。したがって、この触媒反応で見られる Al 助触媒の効果は、倍数の異なる触媒活性種の生成に起因することが示唆された。

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