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Solution XAS Analysis of Various (Imido)vanadium(V) Dichloride Complexes Containing Monodentate Anionic Ancillary Donor Ligands: Effect of Aluminium Cocatalyst in Ethylene/Norbornene (Co)polymerization

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Effects of ligand and ligand substituents in a series of (imido)vanadium(V) complexes containing monodentate anionic ancillary donor ligands of the type, V(NAr)Cl₂(L) [Ar = 2,6-Me₂C₆H₃; L = OAr, O-2,6-Ph₂C₆H₃, N = C[†]Bu₂, 1,3-[†]Bu₂(CHN)₂C = N, WCA-NHC (anionic *N*-heterocyclic carbenes with a weakly coordinating borate moiety)] and V(NAd)Cl₂(OAr) (Ad = 1-adamantyl), were explored by the solution V K-edge XANES (pre-edge and edge region) spectra. No significant differences in the pre-edge (and the edge) peaks were observed between these complexes which fold a distorted 4 coordinate tetrahedral geometry around vanadium; the shoulder-edge peaks ascribed to the presence of V–Cl bonds were also observed in all cases. No significant spectral changes were observed when the phenoxy analogues (exhibiting catalytic activities for ethylene/norbornene copolymerization) were treated with MAO, and even addition of norbornene, suggesting preservation of the oxidation state. Remarkable changes in the XANES spectrum (decrease in the intensity of the pre-edge peak and low-energy shift of the edge region) were observed after addition of AlⁱBu₃ toward V(NAr)Cl₂(WCA-NHC), and no notable changes were observed upon further addition of AlⁱBu₃ and norbornene; these results suggest that the formed species, presumably vanadium(III), act directly as the active species in this catalysis.

Keywords

Vanadium complex catalyst, XANES spectra, Oxidation state, Ethylene copolymerization, Aluminium cocatalyst, Norbornene

1. Introduction

Polyolefins [such as high density polyethylene (HDPE), linear low density polyethylene (LLDPE), and polypropylene (PP)] are important synthetic polymers generally produced by transition metal catalyzed olefin polymerization. Design of more effective molecular catalysts for precise polymerization is very important for the synthesis of new polymers as well as development of more efficient processes^{1)–10)}. Vanadium complex catalysts offer unique characteristics (high reactivity toward olefins) as reported by the classical Ziegler-type vanadium catalyst systems [VOCl₃ and Et₂AlCl, EtAlCl₂, ⁿBuLi etc.]^{7),11)–14)}. (Imido)-

vanadium(V) complexes containing monodentate anionic donor ligands (L) of the type, V(NAr)Cl₂(L) [L = aryloxo (**1a,b**)^{15)–18)}, ketimide (**2**)^{19),20)}, imidazolin-2-iminato (**3**)²¹⁾ etc., **Scheme 1**], are known to exhibit remarkable catalytic activities for the ethylene polymerization^{15)–21)} and the copolymerization with norbornene (NBE)^{16)–18),21)}. Moreover, we recently reported that the (arylimido)vanadium(V) complexes containing anionic *N*-heterocyclic carbenes with a weakly coordinating borate [B(C₆F₅)₃] moiety (WCA-NHC)^{22),23)} of the type, V(NAr)Cl₂(WCA-NHC) [**4**, NHC = 1,3-bis(2,6-dimethylphenyl)-imidazolin-2-ylidene, **Scheme 1**], exhibited remarkably high catalytic activity for ethylene polymerization in the presence of AlⁱBu₃²⁴⁾, which has been considered as an ineffective Al cocatalyst in the metal catalyzed polymerization^{1)–21)}. The activity of **4** in the presence of AlⁱBu₃ for ethylene polymerization was apparently higher than that of **4** in the presence of methylaluminumoxane (MAO), Et₂AlCl cocatalyst²⁴⁾; **4** also efficiently copolymerized ethylene with NBE in the presence of AlⁱBu₃ (**Scheme 1**)²⁵⁾.

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^{51}V nuclear magnetic resonance (NMR) and electron spin resonance (ESR) spectra, and V K-edge X-ray absorption near edge structure (XANES) spectra of the catalyst solution demonstrated that the observed different performances in the presence of MAO and Al^iBu_3 are due to formation of different catalytically active species with different oxidation states²⁵.

Synchrotron X-ray absorption spectroscopy (XAS) is a powerful tool for obtaining structural information about the oxidation state by analysis of pre-edge and edge peaks in XANES analysis, and the coordination atoms around the metal center by FT-extended X-ray absorption fine structure (EXAFS) analysis. XAS is recognized as one of the most effective methods for the study of heterogeneous catalysis^{26)~34)}. However, reported examples of solution XANES spectra, especially of homogeneous (molecular) catalysis have been limited^{25),34)~39)}. Solution XANES analysis can provide information about both oxidation state and structural information *in-situ*^{25),34),36)~39)}, which cannot be obtained by X-ray crystallographic analysis, and can identify both paramagnetic and diamagnetic species (as analyzed by NMR and/or ESR spectra)^{40)~43)}, even “NMR and ESR silent” species³⁴⁾.

Solution XANES spectra of vanadium complexes^{25),34),38),39)} display certain unique characteristics compared to those in the solid state, this study thus describes the XANES spectra of a series of 4 coordinate (imido)vanadium(V) dichloride complexes containing monodentate anionic ancillary donor ligands (shown in **Scheme 1**) to explore the effects of the ligand and the ligand substituents on the spectra (pre-edge and edge peak)⁴⁴⁾, as well as the spectra of the catalyst solutions with the addition of different Al cocatalysts (in the presence of monomers, norbornene)^{15)~20),24),25)} to obtain direct information concerning oxidation of the catalytically active species.

2. Results and Discussion

2.1. Solution XANES Spectra of (Imido)-vanadium(V) Dichloride Complexes Containing Monodentate Anionic Donor Ligands

Figure 1 shows the solution-phase V K-edge XANES spectra (in toluene at 25 °C, 5.46 keV, obtained using synchrotron radiation at SPring-8, BL01B1 beam-line) for a) $\text{V}(\text{NAr})\text{Cl}_2(\text{O}-2,6\text{-R}_2\text{C}_6\text{H}_3)$ [$\text{R} = \text{Me}$ (**1a**), Ph (**1b**), $\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$] and $\text{V}(\text{NAd})\text{Cl}_2(\text{OAr})$ (**1c**, $\text{Ad} = 1\text{-adamantyl}$), and b) $\text{V}(\text{NAr})\text{Cl}_2(\text{L})$ [$\text{L} = \text{OAr}$ (**1a**), $\text{O}-2,6\text{-Ph}_2\text{C}_6\text{H}_3$ (**1b**), $\text{N} = \text{C}^i\text{Bu}_2$ (**2**), $1,3\text{-}^i\text{Bu}_2(\text{CHN})_2\text{C} = \text{N}$ (**3**), WCA-NHC (**4**)]. In the XANES spectra, the valence is often determined by the position of the K- and/or L_1 -edges, and the local symmetry is inferred by the pre-edge peak area of the K- or L_1 -edge spectra, which show $s \rightarrow d$ transitions^{45)~48)}. Moreover, the

Scheme 1 Ethylene (Co)polymerization Using $\text{V}(\text{NAr})\text{Cl}_2(\text{L})$ (**1-4**)-Al Cocatalysts

characteristics of pre-edge peaks in K-edge XANES spectra of 3d transition metals are known to be affected by the selection rule, coordination number, number of d-electrons, and coordination sphere symmetry. Transition of a 1 s electron to 3d orbital gives weak pre-edge peaks due to the electric quadrupole transition for any symmetries. An intense pre-edge peak is assigned to an electric dipole transition to p-character in the d-p hybridized orbital. Mixing of a metal 4p orbital with the 3d orbital strongly depends on the coordination symmetry, and the degree of which is predictable with group theory. Therefore, centered atoms with tetrahedral (T_d) symmetry display large pre-edge peak areas in K- and L_1 -edge XANES spectra.

XANES spectra for $\text{V}(\text{NAr})\text{Cl}_2(\text{O}-2,6\text{-R}_2\text{C}_6\text{H}_3)$ [$\text{R} = \text{Me}$ (**1a**), Ph (**1b**), $\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$] and $\text{V}(\text{NAd})\text{Cl}_2(\text{OAr})$ (**1c**, $\text{Ad} = 1\text{-adamantyl}$) complexes in **Fig. 1a** showed pre-edge peak (and a shoulder peak) [5466.8 (and 5465.3) eV (**1a**), 5467.4 (and 5465.2) eV (**1b**), 5467.2 (and 5465.8) eV (**1c**), respectively] similar to those in $\text{V}(\text{NAr})\text{Cl}_3$ [5466.8 (and 5465.0) eV]²⁵⁾, $\text{V}(\text{NAd})\text{Cl}_3$ [5467.1 (and 5465.6) eV]³⁸⁾. The obtained spectrum was highly reproducible as demonstrated for **1a**. These pre-edge peaks are considered to show a transition from 1 s to 3d + 4p^{45)~48)}, although limited examples of solution V K-edge XANES spectra through synchrotron radiation are available. Moreover, XANES spectra of these complexes (**1a-1c**) showed a shoulder-edge peak (5478.2, 5478.2, 5478.6 eV, respectively), located relatively close to those in $\text{V}(\text{NAr})\text{Cl}_3$,

Fig. 1 Solution-phase V K-edge XANES Spectra (in toluene at 25 °C) for a) $V(NAr)Cl_2(O-2,6-R_2C_6H_3)$ [$R = Me$ (**1a**), Ph (**1b**), $Ar = 2,6-Me_2C_6H_3$] and $V(NAd)Cl_2(O-2,6-Me_2C_6H_3)$ (**1c**, $Ad = 1$ -adamantyl), and b) $V(NAr)Cl_2(L)$ [$L = OAr$ (**1a**), $O-2,6-Ph_2C_6H_3$ (**1b**), $N = C^tBu_2$ (**2**), $N = C^tBuNCH_2$ (**3**), $WCA-NHC$ (**4**)] (Two spectra of **1a** in Fig. 1a are independent runs with different beam times for checking the reproducibility.)

$V(NAd)Cl_3$ (5477.6, 5476.7 eV, respectively). The shoulder-edge peak was ascribed to the V-Cl bond confirmed previously^{34),38)}. Consequently, the substituent in both the imido and the phenoxy ligands did not cause significant differences in the spectra.

XANES spectra of the dichloride complexes containing ketimide ligand, $V(NAr)Cl_2(N = C^tBu_2)$ (**2**)³⁴⁾, imidazolin-2-iminato ligand, $V(NAr)Cl_2[1,3-tBu_2(CHN)_2C = N]$ (**3**), and WCA-NHC ligand, $V(NAr)Cl_2[WCA-NHC]$ (**4**) in Fig. 1b showed pre-edge peak (and shoulder peak) [at 5466.4, 5466.9, 5467.4 eV (and 5465.1 eV), respectively]. The peaks for **4** (5467.4 eV) and **1b**, **1c** (5467.4, 5467.2 eV, respectively) were slightly different (high energy shifted) from that for **2** (5466.4 eV); the peaks for **1a** (5466.8 eV) and **3** (5466.9 eV) are within the range of 5466.4–5467.4 eV. This order ($2 < 1a, 3 < 1b, 1c, 4$) does not agree with the observed chemical shift in the ^{51}V NMR spectra ($4 \ll 2 < 3$)^{20)~22)}. This observed difference is difficult

Fig. 2 Solution-phase V K-edge XANES Spectra (in toluene at 25 °C) for $V(NAr)Cl_2(O-2,6-R_2C_6H_3)$ [$R = Me$ (**1a**), Ph (**1b**), $Ar = 2,6-Me_2C_6H_3$] after Addition of MAO (10.0 equiv.)

to explain at present. As observed in **1a-c** and the trichloride analogues [$V(NAr)Cl_3$, $V(NAd)Cl_3$], complexes **2-4** showed a shoulder-edge peak (5478.2, 5478.1, 5477.7 eV, respectively) were assumed and defined as ascribed to the V-Cl bond^{34),38)}. These results clearly indicate that basic spectral characteristics (pre-edge, shoulder-edge, and edge peaks) are maintained among these complexes (**1a-c**, **2-4**), which all have distorted 4-coordinate tetrahedral geometry around vanadium.

2. 2. Analysis of Catalyst Solution Consisting of $V(NAr)Cl_2(O-2,6-R_2C_6H_3)$ [$R = Me$ (**1a**), Ph (**1b**)], $V(NAr)Cl_2(WCA-NHC)$ (**4**) and Aluminium Cocatalysts by XANES Spectroscopy

We reported previously that $V(NAr)Cl_2(O-2,6-R_2C_6H_3)$ [$R = Me$ (**1a**), Ph (**1b**)] showed moderate catalytic activity for ethylene polymerization (2930, 1090 kg-PE/mol-V h, ethylene 8 atm in toluene at 25 °C) in the presence of MAO cocatalyst¹⁶⁾. These complexes also showed efficient norbornene (NBE) incorporation in the ethylene/NBE copolymerization resulting in high molecular weight copolymers with uniform molecular weight distributions as well as compositions¹⁶⁾.

Figure 2 shows the XANES spectra in toluene solution for complexes **1a,b** after addition of MAO and addition of MAO and NBE. The pre-edge peak in **1a** (5466.8 eV) did not change with addition of either 10 equiv. of MAO (5466.8 eV), or of MAO and NBE (5466.7 eV). Moreover, no significant change in the pre-edge peak in **1b** (5467.4 eV) was observed with addition of 10 equiv. of MAO (5467.0 eV). These results clearly suggest that both the oxidation state and the basic structure (ligand frame work, especially both imido and aryloxo) were maintained after addition of MAO (suggesting that cationic vanadium(V) alkyl species is the active species), as previously demonstrated

Fig. 3 Solution-phase V K-edge XANES Spectra (in toluene at 25 °C) for V(N-2,6-Me₂C₆H₃)Cl₂(WCA-NHC) (**4**) after Addition of MAO (10.0 equiv.) or Al^{*i*}Bu₃ (10.0 equiv. or 100 equiv.) and/or Norbornene (NBE, 10.0 equiv.), and the Spectrum for V(NAd)Cl₂(NMe₂H)₂ is Also Shown for Comparison^{25),39)}

in the ethylene dimerization using (imido)vanadium complexes containing 2-anilido(methyl)pyridine ligands, V(NAd)X₂[2-ArNCH₂(C₅H₄N)] (X = Cl, Me)³⁸⁾, and in ethylene polymerization using V(NAr)Cl₂(WCA-NHC) (**4**)²⁵⁾, as also shown below for comparison.

Figure 3 shows solution phase XANES spectra for V(NAr)Cl₂(WCA-NHC) (**4**) after addition of Al^{*i*}Bu₃ and NBE. Complex **4** exhibited high catalytic activity for ethylene polymerization in the presence of Al cocatalysts²⁴⁾, and the activity with addition of Al^{*i*}Bu₃ (considered as an ineffective Al cocatalyst for olefin polymerization) was higher than that in the presence of MAO²⁴⁾; the catalyst system (**4** and Al^{*i*}Bu₃) was also effective for ethylene/NBE copolymerization²⁵⁾. As reported previously²⁵⁾, no significant differences in the XANES spectrum (pre-edge peaks and edge) from that in **4** were observed after addition of MAO, suggesting that the oxidation state of **4** was preserved after addition of MAO. These results agreed well with both the NMR and the ESR spectra of the toluene solution²⁵⁾.

In contrast, as shown in **Fig. 3**, remarkable changes in the XANES (pre-edge and edge region) spectrum was observed when **4** was treated with 10 equiv. of Al^{*i*}Bu₃²⁵⁾, and the spectrum did not change upon further addition of NBE (10 equiv.). These results clearly suggest that species formed by treatment of **4** with Al^{*i*}Bu₃ are the active species in this catalysis. Moreover, formation of different active species with different oxidation states occurs in the solution containing **4** after addition of MAO and Al^{*i*}Bu₃.

Moreover, the intensity of the edge peak slightly increased with the decrease in the intensity of the pre-edge peak after addition of 100 equiv. of Al^{*i*}Bu₃, whereas no significant changes in the pre-edge peak position and

the edge peak were observed by varying the Al/V molar ratio. Apparent decreases in the intensity of pre-edge peak upon addition of Al^{*i*}Bu₃ clearly suggests certain structural changes in the distorted tetrahedral geometry around vanadium caused by reaction with Al alkyls to form another species by reduction^{25),39)}, and the result suggests that the difference caused by higher percentage of catalytically active species for ethylene (co)-polymerization^{24),25)}. Based on our previous NMR and ESR study of the catalyst solution consisting of **4** and Al^{*i*}Bu₃ [and the low energy shift in the edge peak compared to the related vanadium(IV) complex, **Fig. 3**]^{25),34)}, presumably certain vanadium(III) species were generated by reduction of **4** after addition of Al^{*i*}Bu₃. The results thus clearly and strongly suggest that species formed from **4** by addition of Al^{*i*}Bu₃ preserve the basic structure irrespective of Al/V molar ratios as well as addition of NBE. We think that this is important information for the better understanding of the catalysis.

The present study investigated solution phase V K-edge XANES spectra (in toluene at 25 °C, 5.46 keV) of a series of 4 coordinate (imido)vanadium(V) dichloride complexes containing monodentate anionic ancillary donor ligands as follows, V(NAr)Cl₂(L) [Ar = 2,6-Me₂C₆H₃; L = OAr (**1a**), O-2,6-Ph₂C₆H₃ (**1b**), N = C^{*i*}Bu₂ (**2**), 1,3-^{*i*}Bu₂(CHN)₂C = N (**3**), WCA-NHC (**4**)] and V(NAd)Cl₂(OAr) (**1c**). Although slight differences in the pre-edge peaks were observed, all the spectra showed a pre-edge (5466.4-5467.4 eV) peak in addition to a shoulder-edge (5477.7-5478.6 eV) peak, which is characteristic of the presence of V-Cl bonds³⁴⁾, and no significant differences were observed irrespective of the anionic ancillary donor ligands. The spectra (pre-edge, shoulder-edge, and edge peaks) for **1a,b** did not change after addition of MAO and NBE, clearly suggesting that the oxidation state did not change as observed previously^{25),38),39)}. In contrast, decrease in the pre-edge peak along with low energy shift of the edge peak in the spectrum were observed when **4** was treated with 10 equiv. of Al^{*i*}Bu₃, and the spectrum did not change with addition of NBE; no remarkable changes in the pre-edge and edge peak were observed after further addition of Al^{*i*}Bu₃. The results suggest that generated vanadium(III) species are active in this catalysis under these conditions. We believe that the information should be important for the basic understanding of the catalysis mechanism, although more information is needed concerning the active vanadium(III) species through careful FT-EXAFS analysis of the catalyst solutions.

3. Experimental Section

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 3A 1/16, 4A 1/8, and 13X 1/16) in the drybox under a nitrogen stream, and was passed through an alumina short column under a N₂ stream prior to use. V(NAr)Cl₂(L) [Ar = 2,6-Me₂C₆H₃; L = OAr (**1a**)¹⁵, O-2,6-Ph₂C₆H₃ (**1b**)¹⁵, N = C^tBu₂ (**2**)⁵⁰, 1,3-^tBu₂(CHN)₂C = N (**3**)²¹, WCA-NHC (**4**)²⁴] and V(NAd)Cl₂(OAr) (**1c**)²⁰ were prepared according to published methods. AlⁱBu₃ was purchased from Kanto Chemical Co., Inc., and polymerization grade ethylene (purity > 99.9 %, Sumitomo Seika 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^{14)~21)}.

Analysis of Catalyst Solution by Solution-phase X-ray Absorption Spectroscopy. V K-edge X-ray absorption fine structure (XAFS) measurements were carried out using the BL01B1 beam line at the SPring-8 facility of the Japan Synchrotron Radiation Research Institute (proposal nos. 2016A1455, 2016B1509, 2017A1315). 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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要 旨

アニオン性支持配位子を持つイミド配位二塩化バナジウム(V)錯体の溶液 XAS 分析 —エチレンとノルボルネンとの共重合におけるアルミニウム助触媒の効果—

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単座アニオン性支持配位子を持つ4配位型のイミド配位バナジウムジクロリド錯体, V(NAr)Cl₂(L) [Ar = 2,6-Me₂C₆H₃; L = OAr, O-2,6-Ph₂C₆H₃, N = C'Bu₂, 1,3-'Bu₂(CHN)₂C = N, WCA-NHC (N-heterocyclic carbenes with a weakly coordinating borate moiety) および V(NAd)Cl₂(OAr) (Ad = 1-adamantyl), のトルエン溶液の XANES スペクトルにより, バナジウム原子周辺の局所構造に対する配位子および配位子上の置換基効果を検討した。バナジウム原子周辺のゆがんだ4配位テトラヘドラル構造を有するいずれの錯体においてもプレエッジピークの位置に大きな違いは見られず, バナジウム-塩素結合に帰属される shoulder-edge ピークが観察された。また, (エチレン/ノルボルネン共

重合に活性を有する) フェノキシ配位錯体に MAO やノルボルネンを添加してもスペクトルに大きな変化は見られないことから, この触媒による重合は価数変化を伴わずに活性種が生成することが示唆された。一方, V(N-2,6-Me₂C₆H₃)Cl₂(WCA-NHC) 錯体に AlⁱBu₃助触媒を添加すると顕著な変化 (プレエッジピーク強度の減少とエッジ領域の低エネルギーシフト) が観察され, 3価種の生成が示唆された。このスペクトルは, AlⁱBu₃の添加量の増加でわずかにプレエッジピークの強度に変化が観察されるもののノルボルネンの添加による変化は見られないことから, いったん生成した還元種 (3価バナジウム種) が直接触媒反応に寄与する可能性が強く示唆された。