Solution XAS Analysis for Reactions of Phenoxide-Modified (Arylimido)vanadium(V) Dichloride and (Oxo)vanadium(V) Complexes with Al Alkyls: Effect of Al Cocatalyst in Ethylene (Co)polymerization

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Abstract: V K-edge XANES (XANES = X-ray Absorption Near Edge Structure) spectra of the reaction solution of $V(NAr)Cl_2(OAr)$ (**1**, Ar = 2,6-$Me_2C_6H_3$) with halogenated Al alkyls (Me_2AlCl, Et_2AlCl, $EtAlCl_2$, 50 equiv) in toluene showed low energy shifts (2.6–3.6 eV on the basis of inflection point in the photon energy) in the edge absorption accompanying slight shift to low photon energy in the pre-edge peak (λ_{max} values); a similar spectrum was observed when the reaction of **1** with Me_2AlCl was conducted in *n*-hexane. These results strongly suggest a formation of similar vanadium(III) species irrespective of kind of Al alkyls and solvent (toluene or *n*-hexane). Significant low-energy shifts in the edge absorption accompanied with diminishing the strong pre-edge absorption were also observed when $VOCl_3$ or $VO(O^iPr)_3$ was treated with Me_2AlCl (10 equiv) in toluene, clearly indicating a formation of low oxidation state vanadium species accompanied with certain structural changes (from tetrahedral to octahedral) in solution.

Keywords: vanadium catalyst; XANES; ethylene polymerization; Al alkyls; polymerization mechanism; active species; homogeneous catalysis

1. Introduction

Transition metal catalyzed olefin polymerization plays a key role in commercial production of polyolefin [1–11]. The classical Ziegler-type vanadium catalyst systems (consisting of $VOCl_3$ and halogenated Al alkyls, etc.) displays notable reactivity toward olefins [12–18], and the catalyst system has been used for commercial production of synthetic (ethylene propylene diene monomer, EPDM) rubber [5,11,19–21]. In this catalyst system, large excess of Cl_3CCO_2Et (ETA, called re-oxidant) was required to improve a severe concern of the rapid catalyst decomposition, assumed as due to conversion to the inactive species by reduction; ethylene polymerizations by most of the catalyst systems were thus performed with addition of large excess of ETA [5,11,18–21]. Presence of the active vanadium(III) species have been postulated based on the titration analysis as well as the ESR (electron spin resonance) spectra [22–28]. The approach by ESR spectroscopy (generally employed for analysis of paramagnetic compounds) [24–32] however faces difficulties such as observation of so called "ESR silent" species [V(III) with a $3d^2$ configuration through an interaction of the two unpaired electrons (spin–spin coupling), or an antiferromagnetically coupled V(IV) dimer (spin–orbit coupling), poor structural information in addition to difficulty of the quantitative analysis.

We reported that the phenoxide-modified vanadium(V) dichloride complexes containing arylimido ligand, in particular $V(NAr)Cl_2(OAr)$ (**1**, Ar = 2,6-$Me_2C_6H_3$) [33–35], exhibited high activities for ethylene polymerization and the copolymerization with norbornene (NBE) in the presence of Al cocatalysts (MAO or Me_2AlCl, Et_2AlCl) (Scheme 1). As summarized in Table 1, the activities, the M_n values in the resultant (co)polymers, and the

NBE contents in the copolymers were affected by the Al cocatalyst (and solvent) [34,35]; the activity was decreased by adding ETA [35]. The complex with anionic NHC ligand containing borate moiety (WCA-NHC, **2**) showed the high activities for ethylene polymerization upon the addition of Al^{i}Bu$_3$ [36,37]; the activity by complex **2**–Al^{i}Bu$_3$ showed higher (TOF 653 s^{-1}, 66,000 kg-PE/mol-V·h) than those reported previously [37]. Moreover, the related (adamantylimido)vanadium(V) complex containing 2-(2′-benzimidazolyl)pyridine ligand (**3**) exhibited significant activities for ethylene polymerization in the presence of Me$_2$AlCl, and the activity further increased with addition of ETA [38].

(i) Effect of Al cocatalyst

　　　catalyst **2**: MAO < Al^{i}Bu$_3$

　　　catalysts **1** and **3**: Al^{i}Bu$_3$ *(negligible)* << MAO < Me$_2$AlCl

　　　catalyst **1**: Me$_2$AlCl < MAO *(better NBE incorporation)*

(ii) Effect of Cl$_3$CCO$_2$Et (ETA)

　　　catalyst **1**: Ineffective　　　　　catalyst **3**: Effective
　　　Decrease in the activity　　　　　*Increase in the activity*
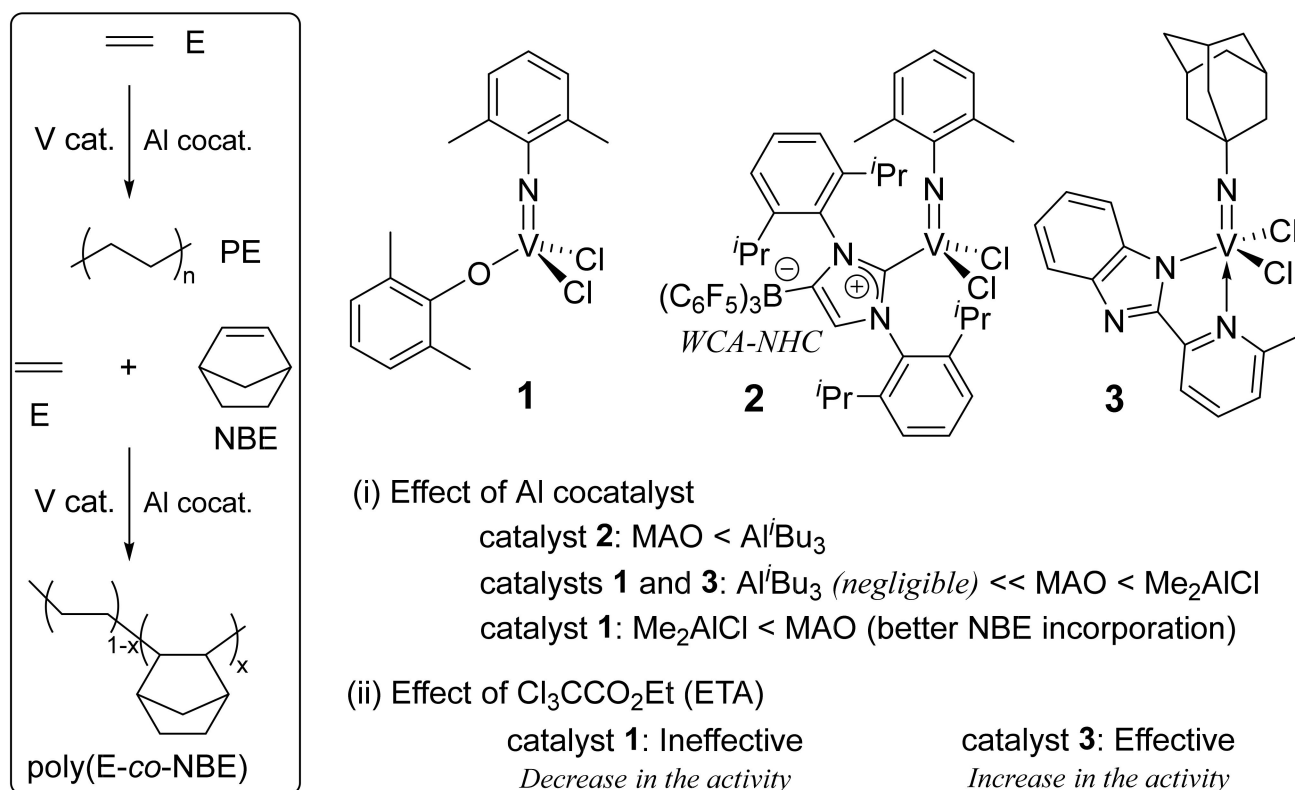
Scheme 1. Selected (imido)vanadium(V) dichloride complex catalysts for ethylene polymerization, ethylene/norbornene copolymerzation [33–38].

Table 1. Effect of Al cocatalyst, solvent and ETA (Cl$_3$CCO$_2$Et) in ethylene polymerization by V(NAr)Cl$_2$(OAr) (**1**, Ar = 2,6-Me$_2$C$_6$H$_3$)—Al cocatalyst systems [35] [a].

Run	Cat.1/μmol	Al Cocat.	Solvent	Activity [b] $\times 10^{-3}$	M_n [c] $\times 10^{-5}$	M_w/M_n [c]	NBE [d] /mol%
2	1.0	MAO	toluene	880	3.02	1.79	23.9
3	0.05	Me$_2$AlCl	*n*-hexane	2400	-	-	-
4	0.05	EtAlCl$_2$	*n*-hexane	47,300	3.56	3.85	-
5	0.05	Me$_2$AlCl	toluene	27,500	89.8 [e]	-	-
6	0.05	Me$_2$AlCl	toluene	23,400	9.56	1.83	15.2
7	0.05	Et$_2$AlCl	toluene	11,700	25.7	1.42	-
9	0.05	EtAlCl$_2$	toluene	37,400	1.98	3.04	-

[a] Conditions: catalyst 0.05 μmol, solvent + cocatalyst solution = total 30 mL, ethylene 8 atm, NBE 0 (runs 1,3–5,7–8) or 15 mmol (runs 2 and 7), 10 min, Al cocatalyst 250 μmol. [b] Activity in kg-polymer/mol-V·h. [c] GPC data in *o*-dichlorobenzene vs. polystyrene standards. [d] NBE content (mol %) estimated by ^{13}C-NMR. [e] Molecular weight by viscosity. [f] Polymerization in the co-presence of CCl$_3$CO$_2$Et (ETA 10.0 equiv to V).

As shown in Figure 1, formations of certain vanadium(III) species (observed as low energy edge shift) by reduction with halogenated Al alkyls (**1,3**) or Al^{i}Bu$_3$ (**2**) accompanying their structural changes (observed as changes in their pre-edge intensities) were suggested

by the V K-edge XANES (X-ray Absorption Near Edge Structure) analyses in toluene (on the basis of reference samples including metal oxides), whereas the oxidation state and the basic coordination geometry were preserved when **1–3** were treated with MAO [37]. The observed facts (structural changes in the XANES spectra) were also supported (assigned each absorptions) by TD-DFT calculation [39,40]. The EXAFS (Extended X-ray Absorption Fine Structure) analysis revealed that the formed species contain the arylimido ligand in all cases. The results also revealed that the species contain *one* neutral V–Cl bond (2.34 ± 0.04 Å) when **2** was treated with Al^{i}Bu$_3$, and that *two* neutral V–Cl bonds were present when the phenoxide analogue (**1**) was treated with Me$_2$AlCl (Table 2). Moreover, the formed species contain *three* neutral V–Cl bonds when **3** was treated with Me$_2$AlCl and the edge intensity increased upon addition of ETA accompanied with decreasing the pre-edge intensity (suggesting the structural change) [37]. The results thus suggest formations of three different V(III) species which possess a different number of coordinating neutral donor (Cl) ligands for the stabilization.
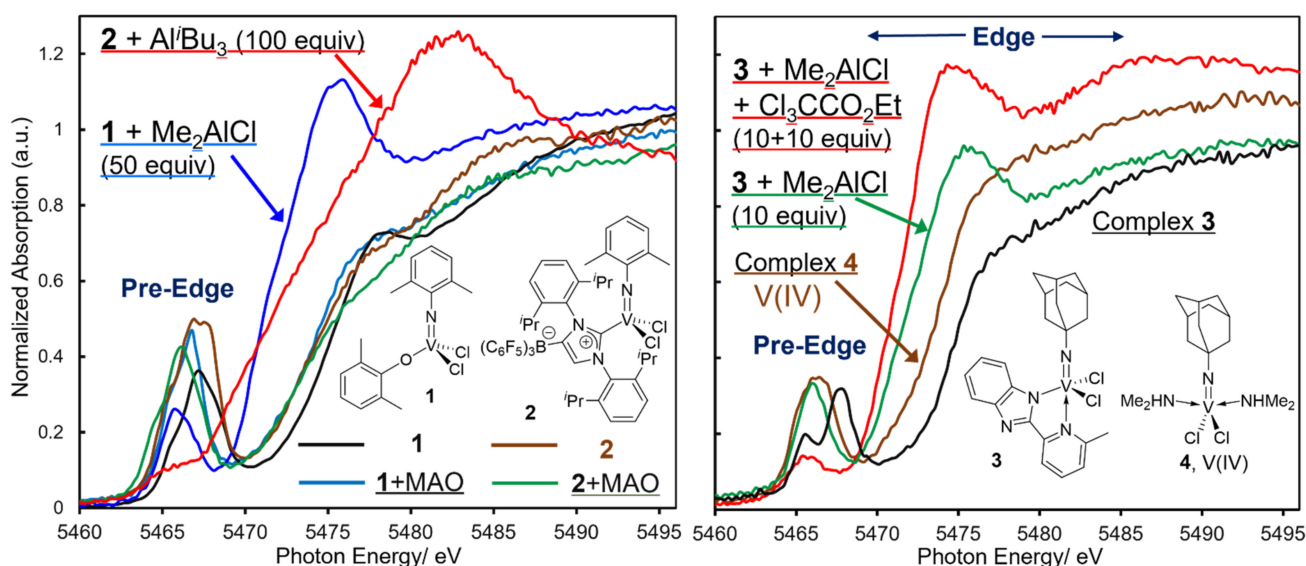
Figure 1. V K-edge XANES spectra (in toluene at 25 °C) for (**left**) V(NAr)Cl$_2$(OAr) (**1**, Ar = 2,6-Me$_2$C$_6$H$_3$) [37], V(NAr)Cl$_2$(WCA-NHC) (**2**) [37], and (**right**) V(NAd)Cl$_2$(L) [**3**, Ad = 1-adamantyl, L = 2-(2′-benzimidazolyl)-6-methylpyridine] [38] in the presence of methylaluminoxane (MAO), Me$_2$AlCl or Al^{i}Bu$_3$.

Table 2. Summary of data for V(NAr)Cl$_2$(OAr) (**1**, Ar = 2,6-Me$_2$C$_6$H$_3$) [37], V(NAr)Cl$_2$(WCA-NHC) (**2**) [37], and V(N-1-adamantyl)Cl$_2$[2-(2′-benzimidazolyl)-6-methylpyridine]) (**3**) [38] in the presence of Me$_2$AlCl or Al^{i}Bu$_3$ (V K-edge EXAFS oscillations and FT-EXAFS spectra in toluene at 25 °C).^{a}·

	Complex 1		1 + Me$_2$AlCl (50 Equiv)		Complex 2		2 + Al^{i}Bu$_3$ (100 Equiv)		Complex 3		3 + Me$_2$AlCl (10 Equiv)	
Atom	C.N.	*r* (Å)	C.N.	*r* (Å)	C.N.	*r* (Å)	C.N.	*r* (Å)	C.N.	*r* (Å)	C.N.	*r* (Å)
N(O)	2.4 (3)	1.80 (5)	1.3 (2)	1.64 (4)	2.1 (2)	1.62 (3)	0.8 (3)	1.66 (17)	1.7 (2)	1.683 (5)	0.9 (3)	1.64 (2)
N									1.2 (8)	2.290 (42)		
Cl	1.9 (2)	2.18 (3)	2.0 (2)	2.45 (3)	1.0 (2) 1.0 (2)	2.16 (4) 2.34 (5)	1.0 (2)	2.34 (4)	1.6 (2)	2.293 (3)	2.6 (1)	2.455 (7)

^{a} Atom: neighbor atom, C.N.: coordination number, *r*: bond length.

As demonstrated in Figure 1, synchrotron X-ray absorption spectroscopy (XAS) provides important information of the oxidation state and the basic geometry (through XANES analysis) and the atoms coordinated to the metal center (through FT-EXAFS analysis) [41–50]. The method has been popular in the study of heterogeneous catalysis [41–46].

We recently demonstrated that the method is also useful for analysis of homogeneous catalysis, especially vanadium and titanium catalysts [40,46,47]. In this paper, we conducted XANES spectral studies for reactions of phenoxide-modified (arylimido)vanadium(V) dichloride (**1**) with different halogenated alkyls (effects of Al cocatalyst, solvent). As, as described above, (oxo)vanadium(V) trichloride, $VOCl_3$, has been used as the catalyst component in the classical Ziegler-type olefin polymerization catalyst, we also studied the solution XANES analysis of $VOCl_3$ and $VO(O^iPr)_3$ treated with Me_2AlCl [51]. We thus herein demonstrate a formation of vanadium(III) species by treating the (oxo)vanadium complexes with Me_2AlCl through the XANES spectra. It was revealed that their photon energies at the edge absorptions were relatively close to those observed in the solutions of complex **1** and **3** treated with Me_2AlCl, but their pre-edge intensities were apparently different. The fact strongly suggests a formation of different vanadium(III) species with different coordination geometry.

2. Results and Discussion

2.1. Solution V K-Edge XANES Spectra of (Oxo)vanadium(V) and (Arylimido)vanadium(V) Complexes

Figure 2 shows V K-edge XANES spectra for $VOCl_3$, $VO(O^iPr)_3$ (in toluene at 25 °C; 5.46 keV, 50 μmol-V/mL; measured in the SPring-8 facility of the Japan Synchrotron Radiation Research Institute (JASRI), the BL01B1 beam line); the spectra for $V(NAr)Cl_2(OAr)$ (**1**, Ar = 2,6-$Me_2C_6H_3$), $V(NAr)(OAr)_3$, reported previously [37], are also placed for comparison.
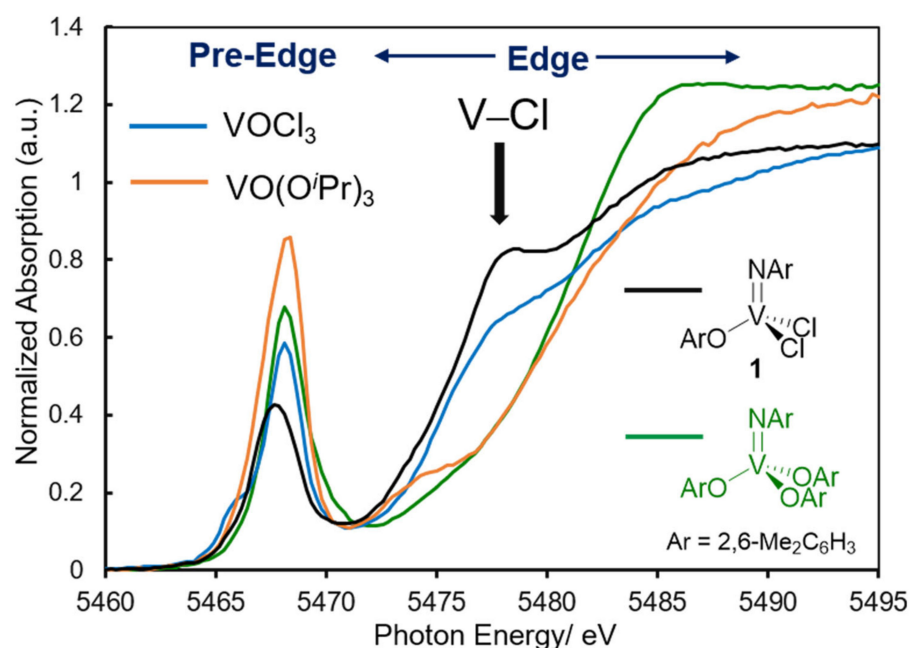
Figure 2. V K-edge XANES spectra for $VOCl_3$, $VO(O^iPr)_3$, $V(NAr)Cl_2(OAr)$ (**1**, Ar = 2,6-$Me_2C_6H_3$), and $V(NAr)(OAr)_3$ (in toluene at 25 °C; 5.46 keV, 50 μmol-V/mL).

The XANES spectra of **1** and $V(NAr)(OAr)_3$ show sharp pre-edge absorption, generally observed in the four coordinates vanadium(V) complexes with tetrahedral geometry, at 5467.6 eV and 5468.1 eV, respectively. The pre-edge absorption is known to be due to a transition from 1s to 3d + 4p [39,40,46–50]. An absorption band (called a shoulder-edge absorption), which corresponds to an absorption of the V–Cl bond in **1** [39,40,46,47,50], was also observed at 5478.5 eV. Similarly, $VOCl_3$ shows the strong pre-edge peak(s) at 5468.1 eV (and 5466.2 eV) and the similar absorption ascribed to the V–Cl bond at 5478.5 eV, whereas $VO(O^iPr)_3$ shows only the pre-edge absorption at 5468.4 eV. A weak absorption was also observed in $VO(O^iPr)_3$ at 5473.3 eV, but the reason is not currently clear.

*2.2. Solution V K-Edge XANES Analysis for Reactions of V(NAr)Cl$_2$(OAr) (**1**, Ar = 2,6-Me$_2$C$_6$H$_3$) and (Oxo)vanadium(V) Complexes with Al Alkyls: Effect of Al Cocatalyst in Ethylene (Co)polymerization*

As described in the introduction (Table 1), the complex **1** showed high catalytic activities for ethylene polymerization and the copolymerization with NBE [33–35] in the presence of Al cocatalyst. It was revealed that the activities and the M_n values in the resultant (co)polymers (and the NBE contents in the copolymers) were affected by the Al cocatalyst and solvent [34,35]; **1**–AlMe$_3$ catalyst system polymerized NBE with ring-opening metathesis mechanism (rather low activity) [33].

Figure 3 shows V K-edge XANES spectra (in toluene at 25 °C) for reactions of **1** with Et$_2$AlCl, Me$_2$AlCl, EtAlCl$_2$, and with AlMe$_3$ (50 equiv), and the spectrum for the reaction with Me$_2$AlCl in *n*-hexane was also placed for comparison. The spectrum for V(NAd)Cl$_2$(HNMe$_2$)$_2$ [52] was also placed for comparison as a reference of (imido)vanadium(IV) dichloride complex; the spectra of vanadium oxides were also used for comparison [40,46,47]. The pre-edge absorption of **1** (5467.6 eV) in toluene shifted slightly to a low energy region when **1** was treated with halogenated Al alkyls (5465.9 eV (Et$_2$AlCl), 5465.7 eV (Me$_2$AlCl), 5466.1 eV (EtAlCl$_2$)); no significant solvent effect was seen when the reaction was conducted in *n*-hexane (5465.9 eV). These results clearly indicate a formation of vanadium(III) species irrespective of the kind of halogenated Al alkyls.
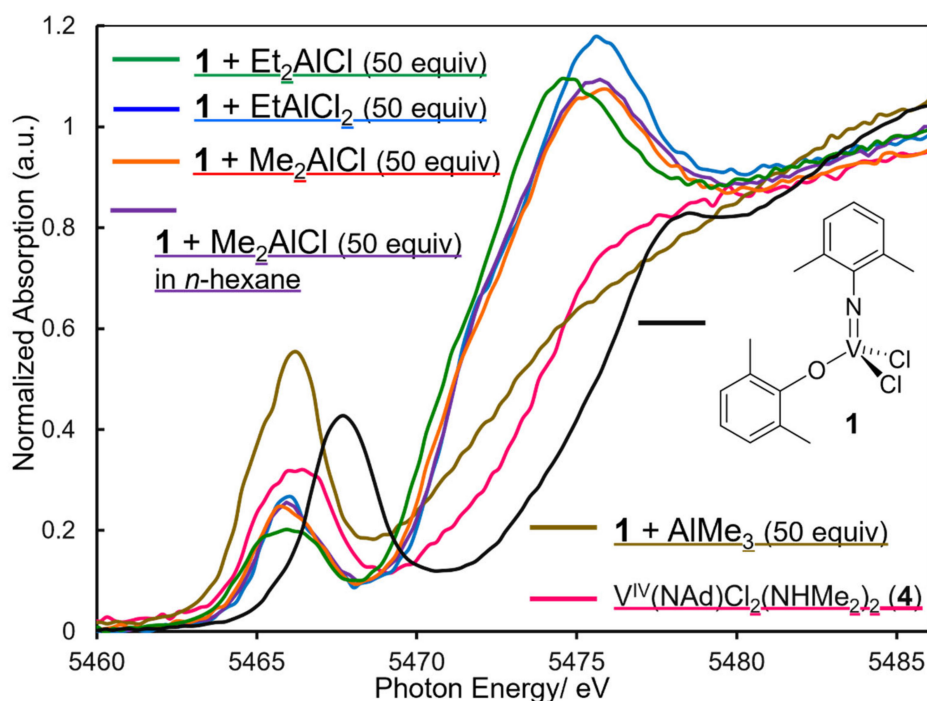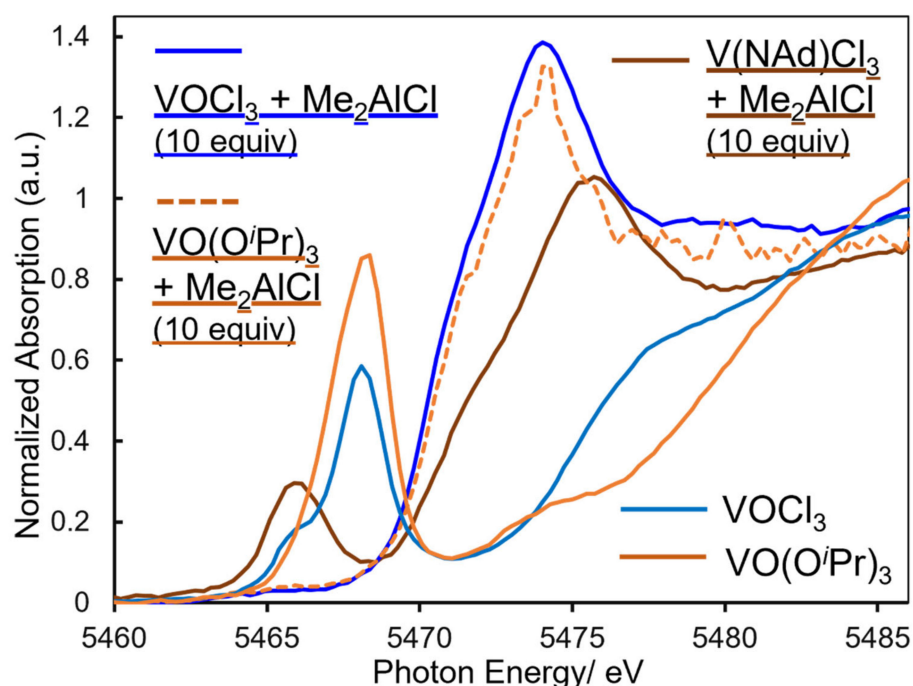

Figure 3. The V K-edge XANES spectra for V(NAr)Cl$_2$(OAr) (**1**, Ar = 2,6-Me$_2$C$_6$H$_3$) in the presence of Et$_2$AlCl, Me$_2$AlCl, EtAlCl$_2$, and AlMe$_3$ (in toluene or *n*-hexane at 25 °C).

The similar low-energy shift in the pre-edge absorption was observed with increase in the intensity when **1** was treated with 50 equiv of AlMe$_3$ (5466.2 eV). The clear low-energy shift in the edge absorption suggests that **1** was reduced by AlMe$_3$ but the shift was not so significant compared to those in the reactions with halogenated Al alkyls (may suggest a formation of vanadium(IV) species); the details are, however, not clear at this moment.

Figure 4 shows V K-edge XANES spectra (in toluene at 25 °C, 50 μmol-V/mL) for reactions of VOCl$_3$ and VO(O^{i}Pr)$_3$ with 10 equiv of Me$_2$AlCl, and the spectrum of the reaction mixture of V(NAd)Cl$_3$ and Me$_2$AlCl, reported previously [53], was also placed for comparison. The XANES spectrum of V(NAd)Cl$_3$ treated with Me$_2$AlCl appeared similar to those for **1** treated with halogenated Al alkyls (Me$_2$AlCl, Et$_2$AlCl, and EtAlCl$_2$, Figure 3),

suggesting a formation of the vanadium(III) species possessing similar oxidations states and the basic structures.

Figure 4. The V K-edge XANES spectra for VOCl$_3$, VO(O^{i}Pr)$_3$ in the presence of Me$_2$AlCl (in toluene at 25 °C).

Note that significant low-energy shifts in the edge absorptions along with disappearance of the pre-edge absorptions were observed when VOCl$_3$ or VO(O^{i}Pr)$_3$ was reacted with Me$_2$AlCl (10 equiv). The pre-edge intensity is known to be influenced by the basic structure (coordination geometry). For instance, the pre-edge intensity in a compound in T_d (tetrahedral) symmetry exhibits much higher than that in the O_h (octahedral) symmetry due to a difference in the degree of a p–d orbital hybridization [39,40,48]. Therefore, the results clearly indicate that both VOCl$_3$ and VO(O^{i}Pr)$_3$ were reduced by Me$_2$AlCl accompanies with structural changes (probably compounds with O_h geometry). The significant shifts in the edge absorptions may suggest a possibility of formation of vanadium(II) species partially, although we do not have the clear evidence at this moment. The formed species in the reaction of VO(O^{i}Pr)$_3$ with Me$_2$AlCl seemed to be unstable (due to observed green slurry after the measurement), a clear spectrum as in the reaction of VOCl$_3$ could not be obtained. The observed difference between VOCl$_3$ and VO(O^{i}Pr)$_3$ may be speculated as due to a difference of number of neutral Cl donor ligands (observed the presence through the EXAFS analysis of **1** and **3** in the presence of Me$_2$AlCl, Table 2) [37,38].

The XANES spectra for toluene solutions of VOCl$_3$, V(NAd)Cl$_3$, the phenoxide complex **1** [37], and V(NAd)Cl$_2$[2-(2′-benzimidazolyl)-6-methylpyridine] (**3**) [38] after treatment with Me$_2$AlCl are summarized in Figure 5. The spectra (edge peak positions and the λ_{max} values) were similar when these (imido)vanadium(V) complexes (**1**, **3**, and V(NAd)Cl$_3$) were treated with Me$_2$AlCl, suggesting a formation of the vanadium(III) species. It was revealed that the addition of Cl$_3$CCO$_2$Et (ETA, 50 equiv) into a toluene solution containing **1**, Me$_2$AlCl, and NBE (50 equiv) led to a decrease in the intensity of the absorption maxima (λ_{max}, at 5475.7 eV), whereas, as reported previously [37], no significant differences in both the peak position and the intensity were observed when **1** was further added NBE (into a toluene solution containing **1**, 50 equiv of Me$_2$AlCl). No significant spectral changes were seen (in the complex and the solution with the addition of Me$_2$AlCl) when the di-isopropylphenyl analogue, V(NAr′)Cl$_2$(OAr′) (Ar′ = 2,6-^{i}Pr$_2$C$_6$H$_3$), was used instead of the dimethylphenyl analogue (**1**) [37]. In contrast, as reported previously, an intensity of

the edge absorption increased with decreasing the pre-edge intensity when **3** was treated with Me_2AlCl and ETA [38]. The fact may explain the fact concerning effect of ETA in the ethylene polymerization; the activity by **3** increased upon the addition of ETA [38] whereas a decrease in activity was seen in **1** with the addition [35]. Different catalytically active vanadium(III) species (with different number of neutral Cl ligands) would thus play roles, as also suggested by the EXAFS analysis (Table 2).
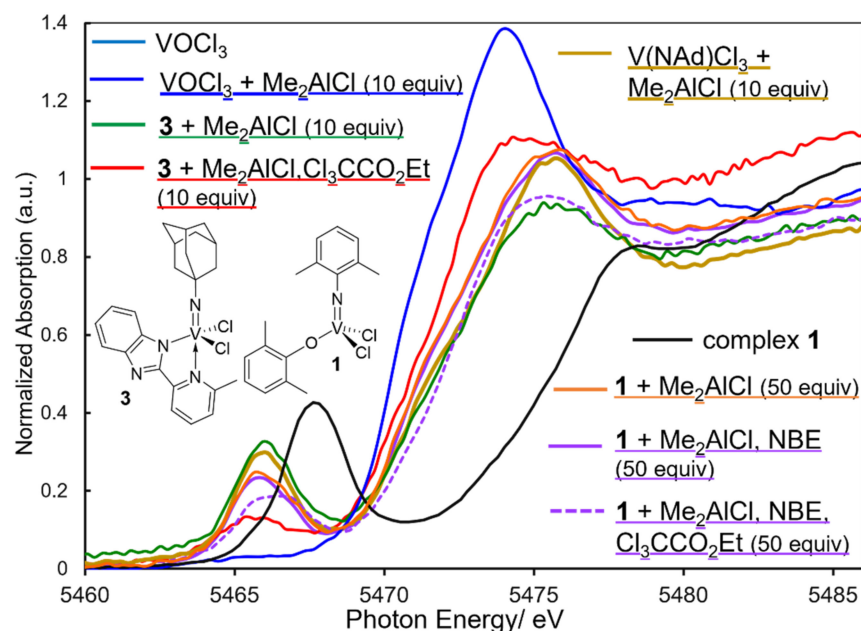
Figure 5. The V K-edge XANES spectra (in toluene at 25 °C) for $VOCl_3$, $V(NAd)Cl_3$ [53], $V(NAr)Cl_2(OAr)$ (**1**) [37], and $V(NAd)Cl_2(L)$ [**3**, L = 2-(2′-benzimidazolyl)-6-methylpyridine] [38] in the presence of Me_2AlCl (and addition of Cl_3CCO_2Et, ETA).

As described above (Figure 4), a significant shift in the edge absorptions with disappearance in the pre-edge absorption was observed when $VOCl_3$ was treated with Me_2AlCl. The fact clearly suggests that $VOCl_3$ was reduced, accompanied with certain structural change (probably from tetrahedral to octahedral). The observed fact is apparently different from those observed in the (imido)vanadium species, in which a V–N bond was preserved even after treatment with Me_2AlCl (Table 2, V–N bond distances: 1.64 Å). The fact also suggests that a different catalytically active (vanadium(III)) species play a role in this catalysis.

3. Materials and Methods

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox. Anhydrous grade toluene and *n*-hexane (Kanto Kagaku Co., Ltd., Tokyo, Japan) were transferred into a bottle containing molecular sieves (a mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in the drybox, and Al reagents (Me_2AlCl, Et_2AlCl, $EtAlCl_2$, and $AlMe_3$ (Kanto Kagaku Co., Ltd.)) were used as received. $VOCl_3$, $VO(O^iPr)_3$ (Sigma-Aldrich, St. Louis, MO, USA), and Cl_3CCO_2Et (Tokyo Chemical Industry, Co., Ltd., Tokyo, Japan) were used as received. $V(NAd)Cl_3$ (Ad = 1-adamantyl) [54], $V(N-2,6-Me_2C_6H_3)Cl_2(O-2,6-Me_2C_6H_3)$ (**1**) [33] were prepared according to a published method.

V K-Edge X-ray absorption near edge structure (XANES) was carried out at the BL01B1 beam line at the SPring-8 facility of the Japan Synchrotron Radiation Research Institute (JASRI, proposal nos. 2016B1509, 2017A1512, 2018A1245, 2018B1335, 2019A1233, and 2020A1473). V K-Edge XAFS spectra of V complex samples (toluene solution, 50 μmol/mL, at 25 °C, a Si (111) two-crystal monochromator was used for the incident beam) were recorded in the fluorescence mode using an ionization chamber as the I_0 detector and 19

solid state detectors as the *I* detector. The X-ray energy was calibrated using V_2O_5, and the data analysis was performed with the REX2000 Ver. 2.5.9 software package (Rigaku Co., Tokyo, Japan). The XANES data was analyzed using a cubic spline from the χ spectra with removal of the atomic absorption background and normalization of them to the edge height.

4. Conclusions

We herein present that the solution V K-edge XANES studies in reactions of (oxo)vanadium(V) and (imido)vanadium(V) complexes with various halogenated Al alkyls (Me_2AlCl, Et_2AlCl, and $EtAlCl_2$), which exhibit remarkable catalytic activities for ethylene polymerization. The formation of certain vanadium(III) species has been demonstrated through the spectral changes by treatment of these vanadium(V) complexes with Al alkyls, whereas, as reported previously [37], no significant changes in either the oxidation state or the basic geometry were observed when these (imido)vanadium(V) complexes were treated with methylaluminoxane (MAO). No significant differences in the spectra were observed in the reaction of $V(NAr)Cl_2(OAr)$ (**1**, Ar = 2,6-$Me_2C_6H_3$) with halogenated Al alkyls, except $AlMe_3$, suggesting a formation of similar catalytically active vanadium(III) species: no significant differences in the spectra were observed when **1** was treated with Me_2AlCl in *n*-hexane.

In contrast, significant low-energy shift with the disappearance of the pre-edge absorption was observed when $VOCl_3$ was treated with Me_2AlCl. The fact clearly suggests a formation of different vanadium(III) species (and may form the species with lower oxidation state partially) in situ. As far as we know, this is the first clear observation of formation of low oxidation state vanadium species in the reaction of $VOCl_3$ with Me_2AlCl in solution through XANES analysis. In addition to the EXAFS analysis, reported previously for **1** and the others [37,38], the information here should be helpful to better understand the catalysis mechanism for olefin polymerization using homogeneous vanadium catalysts. We believe that the solution XAS analysis should be a powerful tool for the study of the catalytically active species, which are very difficult to monitor by NMR and ESR spectra.

Author Contributions: Conceptualization, supervision, project administration, methodology, funding acquisition, writing—original draft, and review and editing, K.N.; formal analysis and investigation, I.I., M.K., K.I., H.A., K.T. and K.N.; and data curation, I.I. and K.N. All authors have read and agreed to the published version of the manuscript.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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