Exploring Oxidation States of the Catalytically Active Species in Ethylene Polymerization/Dimerization Using (Imido)vanadium(V) Complex Catalysts

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Abstract: Studies on exploring oxidation states of the catalytically active species for ethylene dimerization by (adamantylimido)vanadium(V) dichloride complex containing (2-anilidomethyl)pyridine ligand, and for ethylene polymerization by (phenylimido)vanadium(V) dichloride complexes containing 2-(2'-benzimidazol-yl)-6-methylpyridine ligand have been conducted by NMR and ESR spectra, and XAS analysis. It turned out that different active species with different oxidation states play a role depending upon the ligand, Al cocatalyst.
Keywords: XANES, Vanadium complexes, Ethylene.

1. Introduction

Metal catalyzed olefin polymerization/oligomerization is one of the key reactions in chemical industry. Due to attractive characteristics (high reactivity toward olefins) displayed by the classical Ziegler-type vanadium catalyst systems, development of the efficient molecular catalysts has been considered to be an important subject.[1,2] We reported that (adamantylimido)vanadium(V) dichloride complexes containing (2-anilidomethyl)pyridine ligands showed remarkably high both activity and selectivity in ethylene dimerization in the presence of methylaluminoxane (MAO).[3-5] We assumed that the cationic vanadium(V)-alkyl species play a role on the basis of catalytic reactions, NMR and ESR spectra of the catalyst solution. We herein report further study exploring oxidation state of the active species by synthesis and reaction chemistry of the dimethyl complex, NMR spectra and solution XAS analysis of the catalyst sulution.[6] We also report our results for reaction with ethylene using (imido)vanadium(V) dichloride complexes containing 2-(2'-benzimidazolyl)-6-methylpyridine ligand, including effect of Al cocatalysts by NMR and ESR spectra, and by XAS analysis.[7]

2. Experimental

All experiments were carried out under nitrogen atmosphere in a drybox. Reactions with ethylene were conducted in toluene in the presence of d-MAO prepared by removing toluene and $AlMe_3$ from the commercially available MAO (TMAO, Tosoh Finechem Co.). Molecular weights and molecular weight distributions for the resultant polymers were measured by GPC in *o*-dichlorobenzene at 140 °C, and oligomer compositions were analysed by GC. 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 JASRI.

3. Results and discussion

(Adamantylimido)vanadium dichloride complex with (2-anilidomethyl)pyridine ligand, $V(NAd)Cl_2(L)$ [**1**, Ad = 1-adamantyl; L = $2\text{-}(2,6\text{-}Me_2C_6H_3)NCH_2(C_5H_4N)$], exhibited remarkably high activities for selective ethylene dimerization in the presence of MAO [TOF = 911000-2730000 h^{-1} (253-758 sec^{-1}), C_4' = 90.4-97.0 %].[3] In this catalysis, it was demonstrated that a fine tuning of both the imido and the anionic donor chelate ligands plays an essential role.[3,5] Based on NMR and ESR spectra of the catalyst solution (**1** and MAO), ethylene pressure dependence, and effect of Al cocatalyst (MAO *vs* Me_2AlCl), it was strongly suggested that cationic vanadium(V)-alkyl species play a role in this catalysis.[4] In order to explore further mechanistic details, the dimethyl analogue (**2**) was isolated by reaction of **1** with LiMe, and reaction of **2** with 1.0 equiv of $[Ph_3C][B(C_6F_5)_4]$ in Et_2O afforded the cationic complex. The complex **2** exhibited the similar activity/ selectivity (to **1**) in the ethylene dimerization [TOF = 311-425 sec^{-1}, C_4' 97.1-98.4 %].[2] Note that no significant changes in the V K-edge XANES (X-ray Absorption Near Edge Structure) spectra (pre-edge peaks, edge) in toluene solution of **1** and **2** were observed upon addition of MAO (**Figure 1a**). A resonance ascribed to formation of another species was observed in the ^{51}V NMR spectrum by adding MAO. No significant changes in both the EXAFS and the FT-EXAFS spectra were observed in toluene solution containing **1** upon addition of MAO, except that the apparent decrease in the intensity ascribed to V−Cl in **1** was observed by reaction with MAO. It is thus clear that cationic vanadium(V)-alkyl/hydride species play a role in this catalysis.

(Imido)vanadium(V) dichloride complexes containing 2-(2'-benzimidazolyl)-6-methylpyridine ligand (L') of type, $V(NR)Cl_2(L')$ [R = Ad, C_6H_5 (**3**), 2,6-$Me_2C_6H_3$], have been prepared, and their structures were determined by X-ray crystallography as distorted trigonal bipyramidal structures around vanadium (as observed in **1**,**2**). The reactions with ethylene in the presence of MAO afforded a mixture of oligomer and polymers, and the compositions were affected by the imido ligand employed. In contrast, these complexes exhibited high activities for ethylene polymerization in the presence of Me_2AlCl; the phenylimido complex (**3**) showed the highest activity [80100 kg-PE/mol-V·h]. The ethylene copolymerization with norbornene afforded ultrahigh molecular weight copolymers with uniform molecular weight distributions and compositions [ex. $M_n = 1.71\text{-}2.66\times10^6$, $M_w/M_n = 2.27\text{-}2.53$]. On the basis of ^{51}V NMR, ESR and V K-edge XANES spectra of the catalyst solution, the observed difference in the catalyst performance in the presence of between MAO and Me_2AlCl should be due to formation of different active species with different oxidation state. Apparent changes in the oxidation state were observed in the (NMR and XANES, **Figure 1b**) spectra upon addition of Me_2AlCl, whereas no notable spectral changes were observed upon presence of MAO.

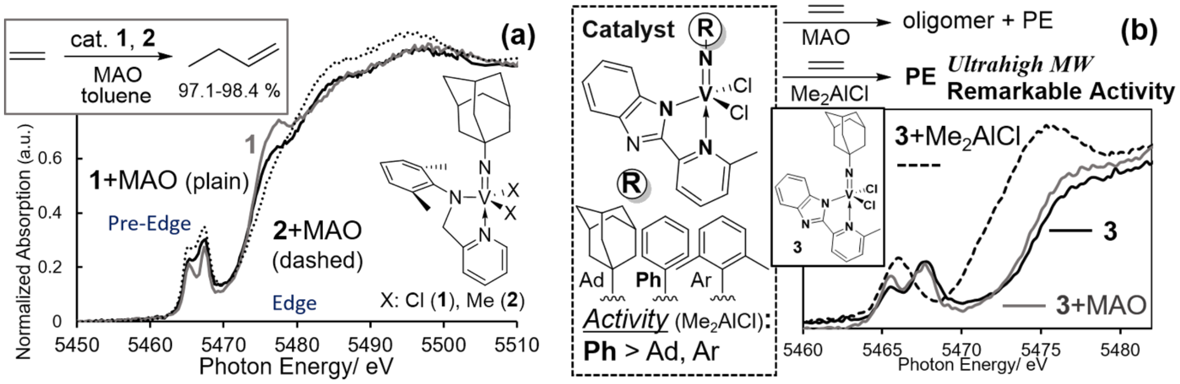

Figure 1. The solution-phase V K-edge XANES spectra (in toluene at 25 ºC) for (a) $V(NAd)X_2(L)$ [X = Cl (**1**), Me (**2**)] upon addition of MAO (10 equiv), (b) $V(NC_6H_5)Cl_2(L')$ (**3**) upon addition of MAO, Me_2AlCl (10 equiv).

4. Conclusions

We have shown that the cationic (adamantylimido)vanadium(V)-alkyl species containing (2-anilidomethyl)pyridine ligand play a role in the ethylene dimerization. In contrast, different active species with different oxidation state were formed as effect of Al cocatalyst (MAO, Me_2AlCl) in the reaction with ethylene using (imido)vanadium(V) complexes with 2-(2'-benzimidazolyl)-6-methylpyridine ligand. We demonstrated that combination of all analyses (NMR spectra, ESR spectra, and XAS analysis) and reaction chemistry should be helpful for providing more clear information for the better understanding.

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