Gas-phase Synthesis of Transition Metal – Ferrocene Clusters by a Two-lasers Ablation Method

Satoshi Nagao, Akiko Kato, Atsushi Nakajima, and Koji Kaya*

Department of Chemistry, Faculty of Science and Technology, Keio University,
3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan
Fax: 81-45-563-5967, e-mail: nakajima@iw.chem.keio.ac.jp
*Institute for Molecular Science, Myodaiji, Okazaki, 444-8585, Japan
Fax: 81-564-55-4386, e-mail: kaya@ims.ac.jp

Vanadium (V) – ferrocene ($FeCp_2$; $Cp = C_5H_5$) clusters, $V_n(FeCp_2)_m$, were produced by a two-lasers ablation method. These species are characterized by mass spectrometry and chemical probe experiments. In the mass spectrum of cationic $V_n(FeCp_2)_m{}^+$, the clusters were produced predominantly at compositions of $(n, m)^+ = (n, n + 1)^+$. These main products showed no chemisorptions reactivity toward NH_3 reactant, showing that clusters having $(n, n + 1)^+$ compositions take a multiple-decker sandwich structure, in which V atoms and $FeCp_2$ molecules are alternately piled up. This result indicates the formation of one-dimensional poly-ferrocene for the first time.
Key words: laser ablation, gas-phase, organometallic complex, ionization energy, poly-ferrocene

1. INTRODUCTION

Since the discovery of ferrocene, $Fe(\eta^5\text{-}C_5H_5)_2$ (or $FeCp_2$ for short), in 1951,[1] organometallic compounds have been a subject of many studies in the past several decade. Numerous derivatives of $FeCp_2$ have been synthesized, and some of them have been utilized as catalysts.[2] In related work, a few reports on the synthesis of triple-decker sandwich complexes composed of transition metal atoms and Cp ligands such as $Ni_2Cp_3{}^+$ (in bulk)[3] and $Fe_2Cp_3{}^+$ (in gas phase)[4] have been known. Interestingly, it has been shown that the one-dimensional compounds exhibit semiconducting or even conducting properties in the solid state.[5,6] Recently, we have successfully produced novel organometallic clusters such as $M\text{-}C_6H_6$,[7] $M\text{-}C_{60}$,[8] (M = Sc, Ti, V) and $Ln\text{-}C_8H_8$[9] (Ln = lanthanide metals) in a gas phase by a combination of laser vaporization and molecular beam methods, and have shown that they can form multiple-decker sandwich structures in which the metal atoms and the ligand molecules are alternately piled up. In these studies, the organic ligands have been restricted to stable molecules in a vapor phase. It is expected that radical ligands such as Cp can make organometallic clusters more stable because the radical ligands can interact with the metal atom much more strongly than the molecular ligands such as C_6H_6 and C_{60}. However, it is generally difficult to prepare only the radical ligand itself in the gas phase, because it is unfeasible to dissociate a precursor molecule uniquely into the corresponding radical without any contamination.

Then, we have developed a new method for the laser vaporization of an organometallic sample containing radical ligands. The laser vaporization method makes it possible to prepare the constituents in considerable density in a short time, and moreover there are no interfering effects of solvents, aggregation phenomena, and counter-ions. The methodology has successfully produced novel gas-phase organometallic clusters composed of ferrocene molecules and transition metal atoms, and has made it possible to include radical ligands in the clusters. Though ferrocene is known as a very stable complex which satisfies the 18-electron rule, we have found ferrocene molecules can surprisingly generate a multi-decker sandwich clusters with a connecting transition metal atom. To our knowledge, the poly-ferrocene composed of ferrocene molecules and transition metals has not been synthesized yet. This proceeding focuses on the formation and the characterization of the one-dimensional poly-ferrocene expressed as $V_n(FeCp_2)_{n+1}$ [$n = 1$–3] by use of two-lasers vaporization and chemical probe methods.

2. EXPERIMENTS

Details of the experimental setup were previously described elsewhere.[8(b),10] Briefly, transition metal (M) – ferrocene ($FeCp_2$) mixed clusters were generated by laser vaporization using two pulsed Nd^{3+}:YAG lasers. Each laser was focused onto the two rotating and translating rods (metal and $FeCp_2$). The energy of the vaporization laser was 10–15 mJ/pulse for the metal rod and 1–4 mJ/pulse for the $FeCp_2$ rod. The hot vapors of the metal and $FeCp_2$ were cooled with a pulsed He carrier gas (5–6 atm stagnation pressure). After the growth of the cluster in a channel, the cluster cations directly produced from laser vaporization were mass-analyzed by a reflectron time-of-flight (TOF) mass spectrometer. To obtain information on the structure of the clusters, the chemical probe of adsorption reactivity was examined by use of the conventional flow-tube reactor.[11] Inside the flow-tube reactor, NH_3 gas was injected in synchronization with the flowing of the clusters, and the NH_3 adducts of the $M_nFe_mCp_k$ clusters were also mass-analyzed. The $FeCp_2$ rod was prepared by pressing $FeCp_2$ powder, which is a similar way for making a C_{60} rod.[8(a)]

3. RESULTS & DISCUSSION

Figure 1 shows a time-of-flight mass spectrum of $V_nFe_mCp_k^+$ cluster cations produced by the laser vaporization of V and $FeCp_2$ targets. Peaks of the cationic clusters are labeled according to the notation, (n, m, k)$^+$, denoting the number of V atoms (n), Fe atoms (m), and Cp ligands (k). Under the prevalent conditions, the contribution of V_n^+ cluster to $V_nFe_mCp_k^+$ formation was negligible because the abundance of the V_n^+ clusters ($n \geq 2$) was less than 1/100 that of the V^+ atoms. The prominent peaks in the mass spectrum correspond to (n, m, k)$^+$ = $(0, 1, 2)^+$, $(1, 2, 4)^+$, $(2, 3, 6)^+$, and $(3, 4, 8)^+$. These compositions are expressed as $V_n(FeCp_2)_{n+1}^+$ [n = 0–4]. The mass distribution of the prominent clusters remained unchanged even when the concentration of V atoms was increased with higher laser fluence for the V rod. It should be noted that almost no dehydrogenated species from $V_n(FeCp_2)_{n+1}^+$ were observed in the mass spectra. When only the $FeCp_2$ rod were vaporized, $FeCp_2^+$ was prominently observed together with minor peaks of $Fe_2Cp_3^+$, and
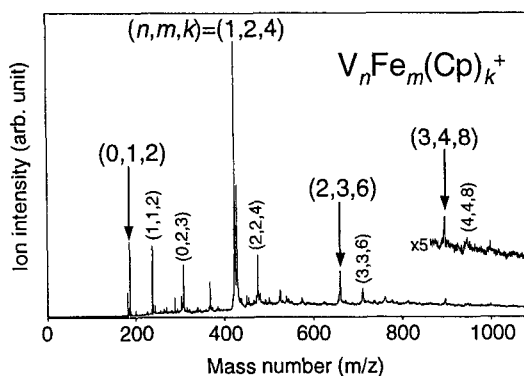

Figure 1. Time-of-flight mass spectrum of V–Fe–Cp (Cp = C_5H_5) cluster cations. Peaks of the cluster cations are labeled according to the notation (n, m, k), denoting the number of vanadium atoms (n), iron atoms (m), and Cp rings (k).

$Fe_3Cp_4^+$. Furthermore, the V–Fe–Cp clusters were produced at (n, m, k)$^+$ = $(1, 2, 4)^+$, $(2, 3, 6)^+$, and $(3, 4, 8)^+$, in which the number of $FeCp_2$ molecules was always by one more than that of V atoms. These results indicate that (1) laser vaporization of the ferrocene rod can generate vapors of $FeCp_2$ and (2) V atoms link the $FeCp_2$ molecules, resulting in the $V_n(FeCp_2)_{n+1}^+$ clusters. Indeed, no products in which metal atoms were exchanged were observed; in a series of k = 4, for example, $(2, 1, 4)^+$ and $(3, 0, 4)^+$ were missing.

To deduce the structure of the V–Fe–Cp clusters by the chemical probe experiment, the reactivity of these abundant clusters toward NH_3 was measured. The $V_n(FeCp_2)_{n+1}^+$ and $FeCp_2^+$ itself were nonreactive toward NH_3, while the other $V_n(FeCp_2)_m^+$ species drastically diminished with the injection of NH_3, resulting in the formation of NH_3 adducts. It is reasonably presumed that an exterior V atom in $V_n(FeCp_2)_m^+$ works as a reaction site toward NH_3 molecules. Thus, no reactivity toward NH_3 reactant for $V_n(FeCp_2)_{n+1}^+$ clearly indicates that each V atom is sandwiched between two $FeCp_2$ molecules.

As described previously,[7] $V_n(C_6H_6)_{n+1}$ clusters also preferably take the multiple-decker sandwich structure in which V atoms and C_6H_6 molecules are alternately piled up. They are observed as main products in the mass spectrum and show no reactivity toward gas reactants. In analogy with these facts, it is the most likely that the abundant and stable
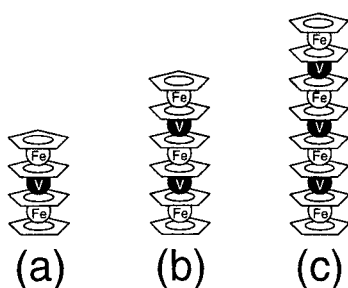
Figure 2. Proposed geometric structures of (a) $V_1(FeCp_2)_2$, (b) $V_2(FeCp_2)_3$, and (c) $V_3(FeCp_2)_4$.

Figure 3. Time-of-flight mass spectrum of Fe–Cp cluster cations produced by the laser vaporization of Fe and FeCp2 targets. Peaks of the cluster cations are labeled according to the notation (m, k), denoting the number of iron atoms (m) and Cp rings (k).

$V_n(FeCp_2)_{n+1}^+$ clusters take the multiple-decker sandwich structures; one-dimensional "poly-ferrocene", as shown in Figures 2(a)–(c), where the V atoms and the FeCp2 molecules are alternately piled up. Generally, transition metal atoms in their ground-state show very low reactivity toward chemical reactants such as CO and C_6H_6.[12] It is suggested that excited-state metal atoms generated by laser ablation might react with FeCp2 molecules, contributing the formation of the poly-ferrocene. From the viewpoint of state selectivity of the metal atom, the formation mechanism for these organometallic clusters should be studied to synthesize them more efficiently.

As well as V–FeCp2 cluster cations, V–FeCp*2 (Cp* = $C_5(CH_3)_5$) cluster cations show almost the same behavior on the mass spectrum; $V_n(FeCp^*_2)_{n+1}^+$ are produced abundantly and they are nonreactive toward NH3. Likewise, the similar patterns of the mass spectra were observed in the mass spectra of Ti–FeCp2 and Ti–FeCp*2 cluster cations. These V–FeCp*2, Ti–FeCp2, and Ti–FeCp*2 cluster cations have also been synthesized for the first time in this work.

As reported previously,[7(a),13] the E_i value of the $V_n(C_6H_6)_{n+1}$ sandwich cluster decreases greatly with the number n; 5.75, 4.70, 4.14, and 3.83 eV for n = 1, 2, 3, and 4 with the growth of the layered sandwich complexes. For $V_n(C_6H_6)_{n+1}$, the one dimensionality leads to the delocalization of d-electron, resulting in the rapid decrease in E_i with size (n). Similarly, the E_i value of the $V_n(FeCp_2)_{n+1}$ clusters also are expected to decrease greatly as n is increased, when d-electrons are delocalized along the molecular axis of the $V_n(FeCp_2)_{n+1}$ clusters. The ionization energy measurement for these clusters is in progress in our
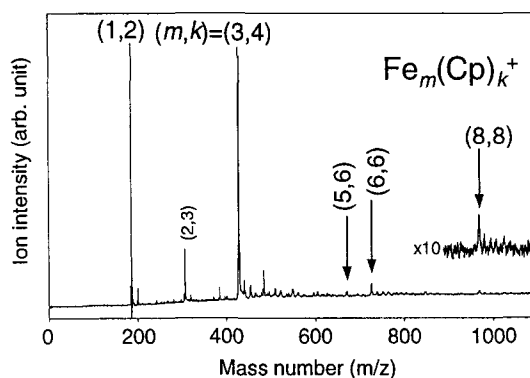
group.

Figure 3 shows a TOF mass spectrum of $Fe_mCp_k^+$ produced by the laser vaporization of Fe and FeCp2 targets. The main products of $Fe_mCp_k^+$ were $(1, 2)^+$ and $(3, 4)^+$. It seems apparent that the $(3, 4)^+$ cluster was formed by the linking reaction between one Fe atom and two FeCp2 molecules. Indeed, the intensity of $(3, 4)^+$ is much stronger than that of $(2, 3)^+$, because there is no way to generate $(2, 3)^+$ from the addition reaction between Fe atoms and FeCp2 molecules. For larger clusters, as shown in Figure 3, the pattern on the mass spectrum is apparently different from that of V–Fe–Cp cluster cations. The $(6, 6)^+$ product is more abundant than $(5, 6)^+$, while $(7, 6)^+$ is less abundant than $(6, 6)^+$. Furthermore, the $(7, 8)^+$ product is scarcely produced. Although the geometric structures of these larger $Fe_mCp_k^+$ cluster cations have been unclear yet, this change in the mass spectrum implies that they do not form the one-dimensional poly-ferrocene favorably.

In summary, we have reported that mixed V–FeCp2 clusters are successfully formed to give multiple-decker sandwich structures of $V_n(FeCp_2)_{n+1}$, which are one-dimensional poly-ferrocene. Although FeCp2 are well-known as a very stable complex which satisfies the 18-electron rule, we have found that these ferrocene derivatives can accept exterior atoms, forming the multiple-decker sandwich clusters. The gas-phase preparation of radical ligands enable us to generate a variety of novel organometallic clusters and would open

up new aspects of photochemistry, electron spin chemistry, and catalytic activity. To obtain information on electronic and magnetic properties of the organometallic clusters, the development of the apparatus to deposite the mass-selected clusters on the substrate without any fragmentations is crucial, which is in progress in our group.

References

[1] T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).

[2] *"Comprehensive Organometallic Chemistry"*, Eds. by G. Wilkinson, F. G. A. Stone, E. W. Abel, Pergamon: New York (1982) Vols. 3–6.

[3] A. Salter and H. Warner, *Angew. Chem. Int. Ed. Engl.*, **11**, 930 (1972).

[4] S. M. Schildcrout, *J. Am. Chem. Soc.*, **95**, 3846 (1973).

[5] T. Kuhlmann, S. Roth, J. Rozière, and W. Siebert, *Angew. Chem. Int. Ed. Engl.*, **25**, 105 (1986).

[6] M. Y. Lavrentiev, H. Köppel, and M. C. Böhm, *Chem. Phys.*, **169**, 85 (1993).

[7] (a) K. Hoshino, T. Kurikawa, H. Takeda, A. Nakajima, and K. Kaya, *J. Phys. Chem.*, **99**, 3053 (1995). (b) P. Weis, P. R. Kemper, and M. T. Bowers, *J. Phys. Chem. A*, **101**, 8207 (1997). (c) T. Kurikawa, H. Takeda, M. Hirano, K. Judai, T. Arita, S. Nagao, A. Nakajima, and K. Kaya, *Organometallics*, **18**, 1430 (1999).

[8] (a) A. Nakajima, S. Nagao, H. Takeda, T. Kurikawa, and K. Kaya, *J. Chem. Phys.*, **107**, 6491 (1997). (b) S. Nagao, T. Kurikawa, K. Miyajima, A. Nakajima, and K. Kaya, *J. Phys. Chem. A*, **102**, 4495 (1998).

[9] (a) T. Kurikawa, Y. Negishi, F. Hayakawa, S. Nagao, K. Miyajima, A. Nakajima, and K. Kaya, *J. Am. Chem. Soc.*, **120**, 11766 (1998). (b) K. Miyajima, T. Kurikawa, M. Hashimoto, A. Nakajima, and K. Kaya, *Chem. Phys. Lett.*, **306**, 256 (1999).

[10] S. Nonose, Y. Sone, K. Onodera, S. Sudo, and K. Kaya, *J. Phys. Chem.*, **94**, 2744 (1990).

[11] M. E. Geusic, M. D. Morse, S. C. O'Brien, and R. E. Smalley, *Rev. Sci. Instrm.*, **56**, 2123 (1985).

[12] J. M. Parnis, S. A. Mitchell, and P. A. Hackett, *J. Phys. Chem.*, **94**, 8152 (1990).

[13] T. Yasuike and S. Yabushita, *J. Phys. Chem. A*, **103**, 4533 (1999).