4P116

Computational Analysis of the XANES Spectra of Vanadium Complexes: A TD-DFT Study

○Jun Yi, Naoki Nakatani, Masahiko Hada, Ken Tsutsumi, Kotohiro Nomura
Department of Chemistry, Tokyo Metropolitan University, Japan

[Abstract]

The X-ray absorption near-edge structure (XANES) of vanadium complexes were observed strongly relative with symmetry, coordination number, oxidation sate, and spin state of the vanadium center. We theoretically investigated the core excitation spectra of vanadium complexes based on the time-dependent density functional theory (TD-DFT) approach to interpret the vanadium K-edge features and to extract information of the electronic structure from the spectra. The calculated V K-edge spectra well reproduced the feature of the experimental spectra of various vanadium complexes. We concluded that the pre-edge peak mainly corresponds to 1s to 3d quadrupole transition in this vanadium complexes and the shoulder peak on the *K*-edge is greatly influenced by pπ* of V-Cl bond.

[Introduction]

Since the 1950s, the Ziegler-type vanadium catalyst systems revealed excellent catalytic performance in olefin reaction, much of the research has focused on the development of high efficiency vanadium complex catalyst.[1] The reactivity of vanadium complexes is often correlated to the oxidation state and site symmetry of the catalyst, therefore, there has considerable interest to get insight into the electronic structure to interpret the reactivity. The XANES of transition metal spectroscopy is a direct method for investigating both the geometry and electronic structure of transition metal complexes [2] because the XANES is sensitive to either the electronic configuration of the target atom or the local geometry around it. Thus, the XANES can be interpreted by collecting fingerprints of the compounds in similar environments.

Recently, Nomura and co-workers have explored the active species of the vanadium complex catalyst in ethylene dimerization by the combination of vanadium nuclear magnetic resonance (NMR) spectrum and vanadium *K*-edge X-ray absorption spectrum.[3,4] The common features can be identified by comparing the fingerprints of sample compound and reference. However, the extraction of more detailed information of the electronic properties and coordination structure is still very difficult only with experimental spectra. In order to interpret the vanadium *K*-edge features and to extract the detailed information of the electronic structure from XANES spectrum, we theoretically investigated the core excitation spectra of vanadium complexes based on the TD-DFT approach.

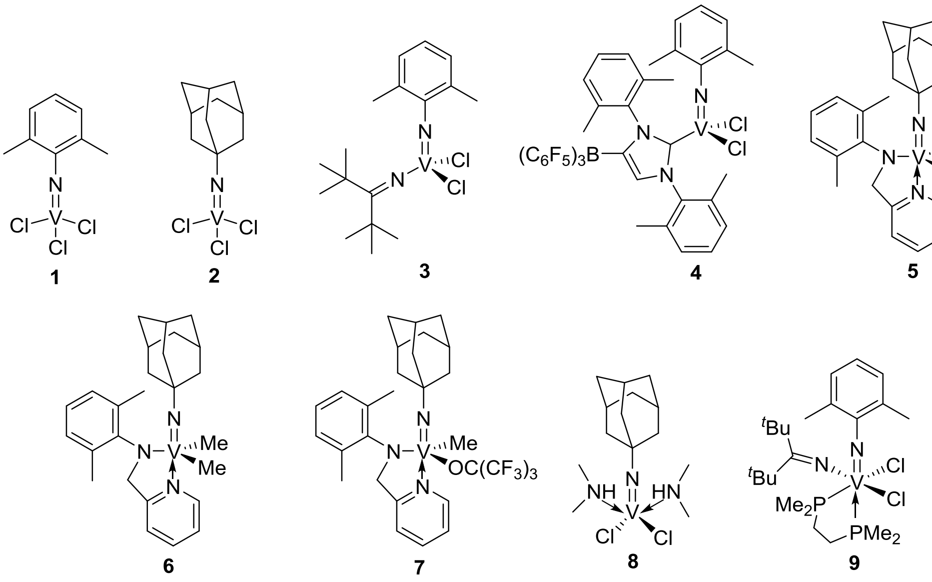
[Methods]

All calculations presented in this work were performed by Gaussian 09 program. Both the geometry optimization and related excitation energy calculation were computed by density function theory (DFT) method. Since the long-range correction is often important in excited state calculations, we have compared the following three functionals: LC-BLYP, CAM-B3LYP and *ω*-B97XD. Because the *ω*-B97XD results give the best agreement with the experimental spectra, we employed the *ω*-B97XD functional, hereafter. For the basis set, we used cc-pVTZ for the vanadium atom and cc-pVDZ for the other atoms. Moreover, the solvation and relativistic effect were considered by polarizable continuum model (PCM) and the second-order Douglas-Kroll-Hess (DKH2) method, respectively.

[Results and Discussion]

We examined 9 kinds of vanadium complexes: 4-coordinate tetrahedral complexes (**1**-**4**), 5-coordinate trigonal bipyramid complexes (**5**-**7**), 5-coordinate distorted square pyramid complex **8**, and 6-coordinate octahedral complex **9**. As shown in Chart 1.

Chart 1. The structure of vanadium complexes.



The calculated spectra well reproduce the features of the experimental vanadium *K*-edge spectra for all the complexes. Fig. 1 shows the calculated XANES spectra of complexes **5**, **6**, and **7**. The complexes **6** and **7** are model complexes for the catalytically active species. The peak intensity in the pre-edge area were calculated to be in the order **6** > **7** > **5**, which are well consistent with those from the experimental spectra. The 1s to 3d-4p mixing dipole transition and 1s to 3d quadrupole transition are expected to contribute to the pre-edge features. Since the shorter metal-ligand bond enhances the 3d-4p mixing, the shorter lengths of the V-C and the V-O bonds than the V-Cl bond explain the stronger peak intensity of complexes **6** and **7** than complex **5**. On the other hand, the 1s to 3d quadrupole transition decreased by the electron-withdrawing ligand of $–OC(CF_3)_3$, thus the peak intensity in complex **7** weaker than complex **6**. The shoulder peak was experimentally observed only for complexes bearing a V-Cl bond, such as complex **5**. Moreover, the calculated results illustrated that the intensity of the shoulder peak for complexes **1** and **2** which contain three V-Cl bond are obviously stronger than the complexes **3**, **4**, **5**, **8** and **9** which have two V-Cl bond. This is because the shoulder peak mainly consists of dipole-allowed 1s to 4pπ* transition of the V-Cl bond.

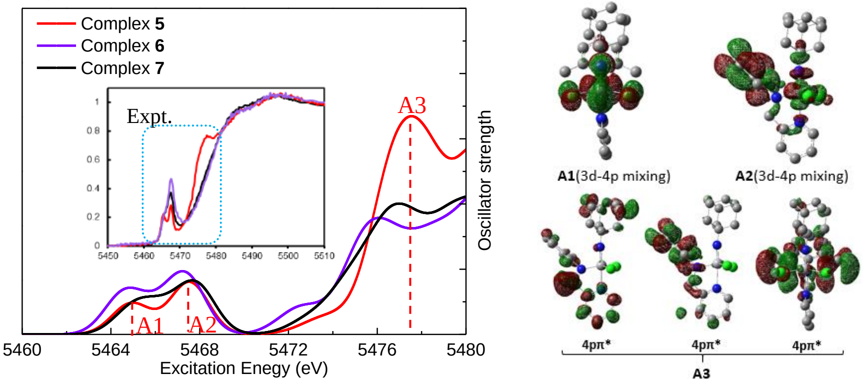


Fig. 1. The calculated vanadium *K*-edge spectra of complexes **5**, **6**, and **7**. Important molecular orbitals of complex **5** which contributes to the XANES spectra were also shown in the right panel.

[References]

[1] K. Nomura *et al. Chem. Rev.* **111**, 2342(2011).

[2] C. H. M. van Oversteeg *et al. Chem. Soc. Rev.* **46**, 102(2017).

[3] K. Nomura *et al. Organometallics* **36**, 530 (2017).

[4] K. Nomura *et al. J. Phys. Soc. Jpn.* **87**, 061014 (2018).