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Vanadium NMR chemical shift in vanadium complex catalyst: a cooperation of QC calculation and MLR analysis

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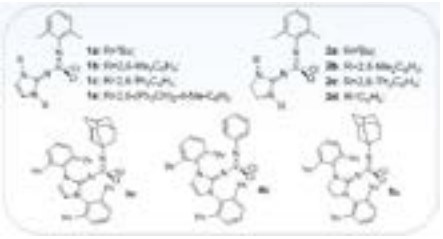
The vanadium complex catalysts play an important role in olefin polymerization. (imido)vanadium(V) complexes containing (2-anilidomethyl)pyridine ligands were presented notable catalytic activity and high selectivity in ethylene dimerization. In recent studies, Nomura and his coworkers found a good relationship between the catalytic activity and the vanadium chemical shift (^{51}V-NMR) for the (imido)vanadium complex in ethylene polymerization. They deduced that the high catalytic reactivity originates from stabilization of the active site by electron-donating substituents. The trend of observed ^{51}V-NMR chemical shifts was well reproduced by the LC-BLYP/cc-pVTZ method as shown in Figure 1. Calculated ^{51}V NMR chemical shifts were analyzed by the multiple linear regression analysis (MLRA) method with a series of calculated molecular properties as shown in Figure 2. We showed an accurate correlation (R^2=0.95) between ^{51}V-NMR chemical shifts and natural charge (Q), HOMO-LUMO energy gap (Δε), and Wiberg bond index of V=N bond (ω).



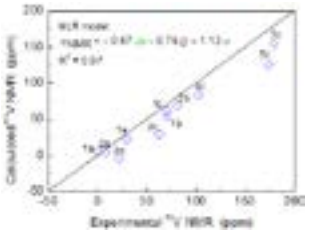


Figure 1: Molecular Structure of Vanadium Complexes [ref. 3]
Figure 2: MLR analysis of V-NMR chemical shifts

Recent Publications

1. X Hou and K Nomura (2016) Ring-opening metathesis polymerization of cyclic olefins by (arylimido)vanadium(v)-alkylidenes: highly active, thermally robust cis specific polymerization. J. Am. Chem. Soc. 138(36):11840.-11849.
2. S Zhang and K Nomura (2010) Highly efficient dimerization of ethylene by (imido)vanadium complexes containing (2-Anilidomethyl)pyridine ligands: notable ligand effect toward activity and selectivity. J. Am. Chem. Soc. 132(13):4960-4965.
3. K. Nomura B K et al. (2014) Synthesis and structural analysis of (imido)vanadium(v) dichloride complexes containing imidazolin-2-iminato- and imidazolidin-2-iminato ligands, and their use as catalyst precursors for ethylene (co) polymerization. Inorg. Chem. 53(1):607-623.
4. Jun Yi et al. (2017) Vanadium NMR chemical shifts of (imido)vanadium(V) dichloride complexes with imidazolin-2-iminato and imidazolidin-2-iminato ligands: cooperation with quantum-chemical calculations and multiple linear regression analyses. J. Phys. Chem. A. 121(47):9099-9105.

Biography

Masahiko Hada is a Professor at Tokyo Metropolitan University, Japan. Previously he worked as Associate Professor at Kyoto University, Japan from 1989-2002. He obtained his PhD from Kyoto University in the year 1986. He has his interests centered around quantum-chemical theories for accurate electronic states of molecules including electron correlation and relativistic effects, and computational approaches for analyses of chemical reactions, spectroscopies and molecular properties. Recently his expertise is extended to 2c-relativistic quantum-chemical theories and its applications to NMR, electronic excited states and spectroscopies (UV, CD, MCD, CPL), and chemical reactions on metal and metal-oxide surfaces, and chemical reaction mechanisms of enzyme containing transition metals.

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