

Grafting Method for Selective Formation of Bis-grafted Surface Species

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Surface organometallics chemistry (SOMC) has been developed as one of attractive approaches to understand surface species in single-site heterogeneous catalysts.¹ In the SOMC, organometallic complexes often grafted by ligand exchange reactions with surface hydroxyl groups on oxide supports (Figure 1, top). However, by this grafting method, the heterogeneity on surface of oxide supports sometimes causes a formation of multiple surface species, which make the characterization of individual surface species difficult. To obtain single surface species, highly dehydroxylated oxide supports, which consist mostly of isolated hydroxyl groups, are frequently used to acquire mono-grafted surface species (Figure 1, bottom). On the other hand, the selective formation of bis-grafted surface species, which are assumed to exhibit different reactivities, have not been accomplished via SOMC.

In order to selectively form bis-grafted surface species on oxide supports, we designed a “pre-grafted precursor” (PGP) bearing a bidentate tetra-*tert*-butoxy disilicate ligand, $-\text{OSi}(\text{O}^t\text{Bu})_2\text{OSi}(\text{O}^t\text{Bu})_2\text{O}-$, which was grafted at silicon atom in the disilicate ligand (Figure 2). Two types of PGP platinum complex were synthesized and identified by NMR spectroscopy and X-ray crystallographic study. Thus-obtained PGPs were grafted on silica supports which were dried at 120 °C in vacuum to remove physisorbed water and the chemical structure of the surface species was evaluated by solid-state NMR spectroscopy. ¹³C CP/MAS NMR spectra showed peaks corresponding to a COD ligand, comparison of chemical shift values to those in a previous report indicated the selective formation of the desired bis-grafted surface species.²

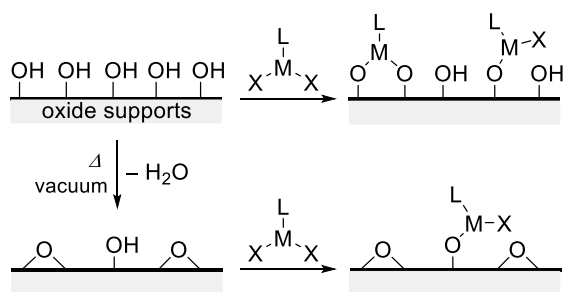


Figure 1. Conventional method to obtain single surface species.

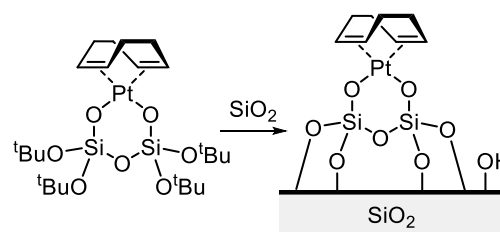


Figure 2. Grafting of pre-grafted precursor.

- 1) C. Copéret *et al.*, *Chem. Rev.* **2016**, *116*, 323. 2) C. Copéret *et al.*, *Dalton Trans.* **2013**, *42*, 238.