Phosphonate-Type Pseudo-Grafted Precursor for Efficient Surface Modification of Silica

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Surface modification of inorganic metal oxides by grafting of phosphonic acids and its derivatives is an attractive approach to obtain tailored organic-inorganic hybrid materials, which can be utilized as heterogeneous catalysts, sensors, etc. However, silica surface is difficult to modify compared to other oxide supports because phosphonic acid derivatives are grafted by slow formation of P–O–Si bonds. On the other hand, we have recently developed "pseudo-grafted precursor" (PGP) bearing disilicate moiety –OSi(O^{t}Bu)$_2$OSi(O^{t}Bu)$_2$O–. PGP can be grafted on silica surface by substitution reaction at the silicon atoms of the disilicate moiety involving the formation of Si–O–Si bonds.[1]

In this work, we developed phosphonate-type pseudo-grafted precursor (P-PGP) to effectively modify the silica surface.[2] P-PGP was synthesized by a reaction of [(^{t}BuO)$_2$Si(OH)]$_2$O with O=P(C$_6$H$_4$OMe)Cl$_2$, and grafted on fumed silica (AEROSIL300) to acquire P-PGP@SiO$_2$. The phosphorous content of P-PGP@SiO$_2$ determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) was 0.40 wt%, which was higher than that of a sample grafting the corresponding phosphonic acid O=P(C$_6$H$_4$OMe)(OH)$_2$ (0.12 wt%). Based on characterization of surface species by solid-state NMR measurement and detection of ^{t}BuOH and isobutene as side-products during the grafting, we propose that the grafting of P-PGP proceeds through the formation of Si–O–Si bonds rather than P–O–Si bonds, which enables the effective surface modification of silica supports.

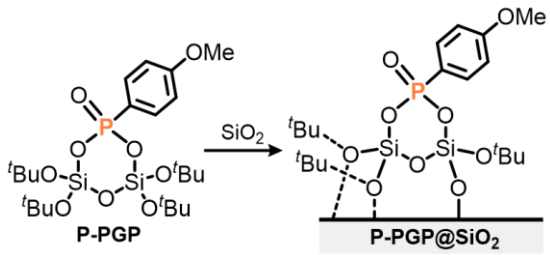

Table 1. phosphorous contents of grafted P-PGP and corresponding phosphonic acid.

Samples	Loaded P (wt%)	Grafted P (wt%)
P-PGP@SiO$_2$	0.50	0.40
O=P(C$_6$H$_4$OMe)(OH$_2$)@SiO$_2$	0.50	0.12

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