An Efficient $PMo_{11}V^{V}O_{40}{}^{4-}$/Silica Material Having Cationic Ammonium Moiety: Synthesis, Characterization, and Catalytic Performance for Oxidation of Alcohols with Dioxygen

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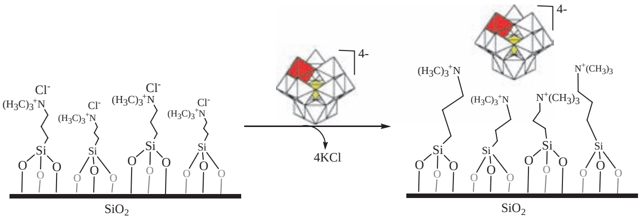
A novel method for grafting transition metal-substituted polyoxometalates (TMSP) onto a modified silica surface was found. Keggin-type vanadium(V)-substituted polyoxomolybdate, $[PMo_{11}V^{V}O_{40}]^{4-}$ (PMoV), was electostatically anchored to a modified silica surface having cationic ammonium moiety. The PMoV-grafted silica material exhibited activities that were higher than those of homogeneous PMoV reactions for oxidation of various alcohols with 1-atm dioxygen in the presence of isobutyraldehyde (IBA).

The isolated well-characterized sites of transition metal-substituted polyoxometalates (TMSP) are well known as active centers for various homogeneous catalytic reactions.[1] An interesting technique to utilize TMSP in heterogeneous systems involves immobilization of TMSP onto oxides using a silane coupling reagent having an amine group, e.g., $[M^{II}(H_2O)PW_{11}O_{39}]^{5-}$ ($M = Co$, Zn) and $[SiW_9O_{37}\{Co^{II}(H_2O)\}_3]^{10-}$ grafted silica,[2] $K_6[SiW_{11}Ni(H_2O)O_{39}]$ grafted silica,[3] and $H_5[PMo_{10}V_2O_{40}]$ grafted MCM-41.[4] However, these materials generally exhibit activities that are lower than those of the original homogeneous reactions because of the deactivation of the transition metal centers in the process of grafting reactions, e.g., the coordination of amine groups to metal centers in TMSP. To prevent the loss of the active metal centers, TMSP could be bound electrostatically to the silica surfaces, e.g., $[(Fe^{III}(OH_2)_2)_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{9-}$/cationic silica nanoparticle, in which TMSP was electrostatically bound on cationic $(Si/AlO_2)^{n+}$ surfaces, displayed better activities for oxidation catalysis compared to those of homogeneous reactions. However, this method was not adequate for the reaction in which anionic TMSP was grafted onto conventional negatively charged or neutral silica.[5]

In this paper, we focused on the Keggin-type phosphovanadomolybdate, $K_4[PMo_{11}V^{V}O_{40}]\cdot 7H_2O$ (PMoV), which is well known for its high catalytic activity in homogeneous oxidation reactions,[6] for the grafting reaction onto a silica surface by electrostatic binding to a silica having cationic quaternary ammonium groups. *N*-trimethoxysilylpropyl-*N*,*N*,*N*-trimethylammonium chloride, $(EtO)_3Si(CH_2)_3N^+(CH_3)_3Cl$ (Azmax), was used as a silane coupling reagent. The reaction in which PMoV was grafted onto silica was carried out as shown in Scheme 1. First, the methoxy groups of the silane coupling reagent reacted cleanly with the hydroxyl groups of silica to eliminate MeOH resulting in the formation of isolated surface species.[7,8] Second, the reaction in which PMoV was grafted onto the modified silica occurred as follows: the modified amorphous silica (1.0 g, 0.27 and 0.39 mmol of $\equiv Si(CH_2)_3N(CH_3)_3Cl$ groups/g) was suspended in water (40 mL) for 30 min. $K_4[PMo_{11}V^{V}O_{40}]\cdot 7H_2O$ (1.03 g, 0.5 mmol) was dissolved in water (50 mL) and this solution was then added to the suspension of silica. The resulting mixture was stirred at 25 °C for 24 h. The solid product was collected, washed with water (30 mL × 3), and then dried under reduced pressure for 2 h. It should be noted that the obtained samples were still yellow after washing with water, indicating that the anionic PMoV interacted strongly with the silica surface. According to elemental analysis,[9] the loadings of PMoV were found to be 0.057 and 0.082 mmol/g, respectively, when 0.27 and 0.39 mmol $\equiv Si(CH_2)_2N(CH_3)_3Cl$ groups/g silica materials were used. Potassium atom was not observed in any of the $PMoV/SiO_2$ samples, indicating that the four potassium counter-ions of PMoV were ion-exchanged by four cationic ammonium moieties to form $[\equiv Si(CH_2)_3N^+(CH_3)_3]_4[PMo_{11}V^{V}O_{40}]$ and four molecules of KCl. The grafted PMoV can be removed by the addition of tetrabutylammonium bromide (TBABr) to form $TBA_4[PMo_{11}V^{V}O_{40}]$, suggesting that there is no covalent bonding between the vanadium site and the ammonium groups.[10] The BET surface areas of 0.057 and 0.082 mmol/g PMoV–SiO_2 were 140 and 141 m^2/g, respectively, which were almost the same as those of the modified silica.[7] Solid-state ^{31}P NMR spectrum of 0.057 and 0.082 mmol/g PMoV–SiO_2 showed a singlet at −4.40 ppm (half width: 84.2 Hz) and at −4.40 ppm (74.0 Hz), which showed a slight shift from the starting PMoV singlet at −4.03 ppm (40.0 Hz), suggesting the existence of electrostatic interaction between the anionic PMoV and the cationic ammonium moiety. The sharp signal suggested that PMoV might be isolated on the silica surface. DR-UV–vis spectra of 0.057 and 0.082 mmol/g PMoV–SiO_2 samples showed an intense band at 315 nm and a weak broad band at 480 nm, which were attributed to a charge-transfer (CT) band of Mo–O and V–O, respectively.[1a] The sharp CT band of Mo–O also indicated that the PMoV species were isolated on the silica surface.[11]

The oxidation of various alcohols with 1-atm dioxygen in the presence of IBA at 85 °C, catalyzed by PMoV–SiO_2 materials, was monitored by GC (TCD, capillary column DB–FFAP, 0.53 mm × 15 m) and HPLC (Shim-pack VP-ODS 150 mm L × 4.6 mm ID (Table 1). During the course of the reaction, the color of the catalyst changed from yellow to green owing to the redox of V^V to V^{IV}, indicating that the reaction mechanism might be the same as that of the $PMo_{10}V_2$-MCM-41/O_2/IBA system, in which an acyl peroxo intermediate was formed by the reaction of IBA with O_2 via a reduction of V^V to V^{IV}, and the intermediate oxidized substrates. In addition, $PMo_{10}V_2$ inhibited the



Scheme 1.

Table 1. Catalytic activities for oxidation of alcohols with 1-atm dioxygen catalyzed by PMoV and PMoV grafted SiO_2[a]

Alcohol /mmol	Catalyst	TON[b]	Product /selectivity/%
benzyl alcohol	PMoV	54	benzaldehyde (>99)
(48.4)	PMoV–SiO_2	153	(>99)
	PMoV/SiO_2[c]	21	(>99)
	PMoV–SiO_2[d]	152	(>99)
1-octanol	PMoV	22	octyl aldehyde (>99)
(6.34)	PMoV–SiO_2	117	(>99)
cyclohexanol	PMoV	21	cyclohexanone (>99)
(9.40)	PMoV–SiO_2[e]	84	(>99)

[a]Reaction conditions: PMoV 20 μmol, PMoV–SiO_2 (0.082 mmol/g, 5 μmol of PMoV), CH_3CN 3–8 mL, alcohol 6.34–48.4 mmol, IBA 11.0–37.6 mmol, $P(O_2) = 1$ atm, reaction temperature 85 °C. [b]Turnover number (TON) after 168 h. [c]PMoV/SiO_2 (0.082 mmol/g, 5 μmol of PMoV) was used. [d]Water (5 mL) was used as a solvent. [e]PMoV–SiO_2 (0.057 mmol/g, 5 μmol of PMoV) was used.

autoxidation of the oxidative products.[4] The carbonyl products were observed with high selectivities (>99%). The turnover numbers (TON = (mole of products)/(mole of catalyst)) were much higher than those of the homogeneous TBA salt of PMoV reactions, and of the mixture of K salt of PMoV and SiO_2 (referred to as PMoV/SiO_2 in Table 1). Furthermore, the catalytic activity of PMoV–SiO_2 in water (TON = 152) was similar to that in acetonitorile (TON = 153) for the oxidation of benzyl alcohol.

To determine whether the active species leached into the solution during a typical catalytic reaction, a sample of 0.057 mmol/g PMoV–SiO_2 and IBA with 1-atm dioxygen was heated to 85 °C for 168 h, and the mixture was filtered while still hot. The color of the filtrate was pale-yellow, suggesting that the surface PMoV species had slightly leached into the solution; however, the leached PMoV species could be neglected in catalytic activities of heterogeneous oxidation reactions. Using the solid after filtration as a catalyst, the oxidation of cyclohexanol was carried out at 85 °C. The TON in the second use (82 after 168 h) was similar to that in the first use (84 after 168 h).[12] In addition, the filtrate showed little activity (0.13% conversion after 168 h). Thus, the PMoV–SiO_2 was reusable as a heterogeneous oxidation catalyst.

In conclusion, the procedure presented in this paper, using PMoV as an example, is one of the more effective methods for anchoring TMSP to the surface of silica supports. Thus, this work appears to support the view that designed chemical reactions of TMSP on a solid surface offer considerable potential for generating effective catalytic sites with TMSP-based structures.

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References and Notes

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7 Amorphous silica (Azmax, 200 m^2/g) was dried at 25 °C under vacuum for 2 h as a pretreatment (4.67 OH groups/nm^2, 1.55 mmol OH groups/g). The number of OH groups were measured by the published method [K. L. Fujdala and T. D. Tilley, *J. Am. Chem. Soc.*, **123**, 10133 (2001)]. 1.0 g of the dried silica support was dispersed in 80 mL of methanol. 0.28, 2.78, and 8.34 mL (0.5, 5.0, and 15.0 mmol) of 50% methanol solution of $(EtO)_3Si(CH_2)_3N(CH_3)_3Cl$ was added to this. This mixture was refluxed at 80 °C for 6 h. The obtained white powder was collected, washed with methanol (10 mL × 3), and then dried under vacuum for 2 h. Anal. [using 0.5 mmol of silane coupling reagent] Found: C, 1.93; H, 0.16; N, 0.42%. Calcd for $(SiO_2)_{59}(Si(CH_2)_3N(CH_3)_3Cl)$ (0.27 mmol $\equiv Si(CH_2)_3N(CH_3)_3Cl$ groups/g of silica): C, 1.94; H, 0.41; N, 0.38%. BET surface area: 138 m^2/g. Anal. [using 5.0 mmol of a silane coupling reagent] Found: C, 2.81; H, 0.20; N, 0.75%. Calcd for $(SiO_2)_{40}(Si(CH_2)_3N(CH_3)_3Cl)$ (0.39 mmol $\equiv Si(CH_2)_3N(CH_3)_3Cl$ group/g of silica): C, 2.81; H, 0.59; N, 0.55%. BET surface area: 130 m^2/g. Anal. [using 15.0 mmol of silane coupling reagent] Found: C, 2.90; H, 0.35; N, 0.50%. Calcd for $(SiO_2)_{43}(Si(CH_2)_3N(CH_3)_3Cl)$ (0.36 mmol $\equiv Si(CH_2)_3N(CH_3)_3Cl$ groups/g of silica): C, 2.62; H, 0.55; N, 0.51%. Thus, the maximum loading of the silane coupling reagent was 0.39 $\equiv Si(CH_2)_3N(CH_3)_3Cl$ groups/g of silica.

8 The three possibilities of structural formation involve one ($-Si(OEt)_2(CH_2)_3N(CH_3)_3Cl$), two ($=Si(OEt)(CH_2)_3N(CH_3)_3Cl$), or three ($\equiv Si(CH_2)_3N(CH_3)_3Cl$) bonding interactions between the silane coupling reagent and the OH groups on the silica surface. According to elemental analysis, the maximum loading of cationic ammonium groups onto an amorphous silica sample was 0.39 mmol/g. This can be compared to the predicted maximum silane coupling reagent loading based on one (1.55 mmol/g), two (0.78 mmol/g) and three (0.52 mmol/g) bonding interactions. On the basis of these comparisons, we concluded that the structure of the surface-bound silane coupling reagent species was well represented by $\equiv Si(CH_2)_3N(CH_3)_3Cl$ groups.

9 Anal. [using the modified silica containing 0.27 mmol of $\equiv Si(CH_2)_3N(CH_3)_3Cl$ groups/g] Found: N, 0.66; P, 0.16; Si, 38.3; Cl, <0.02; K, <0.01%. Calcd for $\{(SiO_2)_{59}\}(Si(CH_2)_3N-(CH_3)_3)_4(PMo_{11}VO_{40})(H_2O)_{15}$ (0.057 mmol PMoV/g): N, 0.32; P, 0.18; Si, 38.4%. Anal. [using the modified silica containing 0.39 mmol of $\equiv Si(CH_2)_3N(CH_3)_3Cl$ groups/g] Found: N, 0.50; P, 0.17; Si, 37.9; Cl, 0.21; K, <0.01%. Calcd for $\{(SiO_2)_{40}\}-(Si(CH_2)_3N(CH_3)_3)_4(PMo_{11}VO_{40})(H_2O)_5$ (0.082 mmol PMoV/g): N, 0.46; P, 0.25; Si, 37.54%.

10 The elemental analysis results were consistent with the composition of $TBA_4[PMo_{11}V^VO_{40}]$. Found, C 27.89; H, 5.17; N, 2.09%. Calcd; C, 27.98; H, 5.28; N, 2.04%.

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12 A solid-state ^{31}P NMR spectrum of the solid, which has been re-oxidized by O_2 at 55 °C for five days, showed a singlet at around −4 ppm with 71.4 Hz of half-width. A solid-state ^{13}C NMR spectrum showed four peaks at 17.6, 69.7, 131.9, 166.0 ppm. There results were almost the same as those of as-prepared PMoV–SiO_2.