Modification of Silica Surfaces by Metallasiloxanes Containing Mo and Ti: Evidence for Concurrent Metal and Ligand Chemisorption

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The molecular metallasiloxanes $Mo(N^tBu)_2(OSiMe_3)_2$ **1**, and $Ti(OSiMe_3)_4$, **2**, both react with the hydroxyl groups on partially dehydroxylated silica surfaces. The amount of chemisorbed metal corresponds, in both cases, to one-half the number of available surface hydroxyl groups. Unlike grafting reactions of metal alkoxides, the chemisorptions are not accompanied by release of protonated ligands. The siloxide ligands are transferred to the silica where they are bound via siloxane or "glass bonds", as in $\equiv SiOSiMe_3$, **3**. By ^{13}C and ^{29}Si CP/MAS NMR, two distinct signals for trimethylsiloxide groups were observed. One is assigned to **3** by comparison to an authentic sample, while the second corresponds to trimethylsiloxide ligands coordinated to grafted metal complexes. The latter are susceptible to protonolysis, while **3** is not. The proposed grafting mechanism involves reaction of **1** or **2** with a single surface hydroxyl to form a chemisorbed metal complex and $HOSiMe_3$, followed by rapid condensation of the silanol with a second surface hydroxyl to generate **3**. Molecular metallasiloxanes are suggested as single-source precursors to metal catalysts supported on alkylsilane-capped surfaces.

Introduction

Silica is widely used as a chromatographic and catalytic support material because of its high surface area and thermal and chemical stability. Hydroxyl-terminated silica surfaces can be rendered hydrophobic by either high-temperature treatment or chemical modification. The latter usually involves reaction with a silylating agent such as $SiCl_xR_{4-x}$, $Si(OR)_xR_{4-x}$, or $(Me_3Si)_2NH$. Displacement of HCl, ROH, or NH_3, respectively, leads to chemisorbed alkylsilane fragments, although the reactions are complicated by self-condensations and chlorination of silica.[1−3]

Residual hydroxyl groups which persist after grafting of metal complexes on the silica surface are deemed responsible for the mobility of supported metal fragments, mediated by the facile migration of surface protons.[4−6] This phenomenon reduces site isolation of supported metal catalysts, which is desirable to prevent coordinatively unsaturated active sites from undergoing aggregation and consequent loss of activity.[7] One approach to inhibiting mobility is to perform postmodification "capping" of residual hydroxyl groups.[8] Ideally, each active site should be surrounded by hydrophobic trimethylsiloxy sites which prohibit its migration. The effectiveness of this procedure depends on the efficiency of the capping or silylating agent and its selectivity toward reaction with the silica hydroxyl groups rather than with the supported metal complexes.

A grafting mechanism which places two identical or different chemisorbed groups on adjacent sites is the cleavage of siloxane bonds. However, because of the low reactivity of ordinary siloxane sites on silica,[2] such reactions are generally limited to complexes of highly oxophilic metals (e.g., $AlMe_3$[9] or $TiCl_4$[10]) or grafting on highly reactive siloxane sites[11,12] created by extreme temperature treatments (~1000 °C).[13,14] For example, reactions of mixed alkylalkoxysilanes with strained siloxanes generate pairs of alkoxysilane sites:[15]

$$R'_nSi(OR)_{4-n} + \equiv SiOSi\equiv \rightarrow \equiv SiOSiR'_n(OR)_{3-n} + \equiv SiOR \quad (1)$$

Recently, the modification of MCM-41 with rare earth

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bis(dimethylsilylamides) was shown to result in the transfer of dimethylsilyl groups to the surface via condensation on surface hydroxyl groups of the HN-$(SiHMe_2)_2$ liberated during grafting,[16] in a process suggested to resemble the well-known reaction of silica hydroxyls with hexamethyldisilazane.[2]

Metallasiloxanes are extensively studied as structural models for silica-supported metal catalysts.[17] Since their volatility often rivals that of analogous metal alkoxides used for chemical vapor deposition, we investigated the preparation of supported metal catalysts using metallasiloxane sources. In the course of this study, we discovered that the adhesion mechanism for metallasiloxanes diverges from the simple ligand metathesis mechanism observed for metal halides and alkoxides.[18] Siloxide ligands displaced as silanols react at surface hydroxyl groups with formation of strong siloxane bonds.

Experimental Section

$Mo(N^tBu)_2(OSiMe_3)_2$ was synthesized according to a published procedure and purified by recrystallization or sublimation.[19] $Ti(OSiMe_3)_4$ was purchased from Gelest and purified by sublimation. A nonporous fumed silica (Degussa Aerosil-200, 200 m^2/g) was used as the oxide support in all experiments.

All IR experiments were performed in sealed all-glass high vacuum reactors (volume ~300 mL), onto which KCl windows were attached with TorrSeal (Varian) for in situ infrared spectroscopy. Transmission spectra were recorded on a dry air purged Mattson Research Series FTIR spectrometer equipped with a DTGS detector. For both background and sample spectra, 32 scans were recorded at a resolution of 2 cm^{-1}.

To begin the experiment, the silica (either pressed into a self-supporting disk or pressed then ground into a fine powder) was dehydrated and partially dehydroxylated under dynamic vacuum at 200 or 500 °C, to give materials subsequently referred to as silica(200) and silica(500), respectively. This treatment does not change the surface area of the silica, but it standardizes the number of surface hydroxyl groups to 2.6 OH/nm^2 (0.86 mmol OH/g) in the case of silica(200) or 1.2 OH/nm^2 (0.40 mmol OH/g) in the case of silica(500).[2] Following thermal treatment, the metal complex was sublimed onto the silica at room temperature, using break-seal techniques to avoid breaking vacuum.[20] After several hours of reaction at room temperature, unreacted physisorbed material was desorbed to a liquid N_2 trap.

For NMR experiments, the modified silica was prepared in powdered form in a Schlenk tube equipped with a high vacuum stopcock and 5 mm o.d. Pyrex NMR tubes welded onto the main body of the Schlenk tube at right angles. Approximately 50 mg of sample were transferred into each attached NMR tube without breaking vacuum, and the tubes were sealed off at 30 mm lengths. The tubes were then placed in zirconia rotors accommodating 5 × 30 mm Pyrex tubes and balanced, if necessary, with Teflon tape. The ^{13}C and ^{29}Si CP/MAS (cross polarization/magic angle spinning) NMR spectra, frequency 50.32 and 39.75 MHz respectively, were recorded on a Bruker ASX-200 spectrometer. Spectra were collected using a 4.4 ms 90° proton pulse with a contact time of 2 ms and relaxation delay of 2 s in the case of ^{13}C and with a contact time of 1 ms and relaxation delay of 1 s in the case of ^{29}Si, both at a spin rate of 4 kHz.

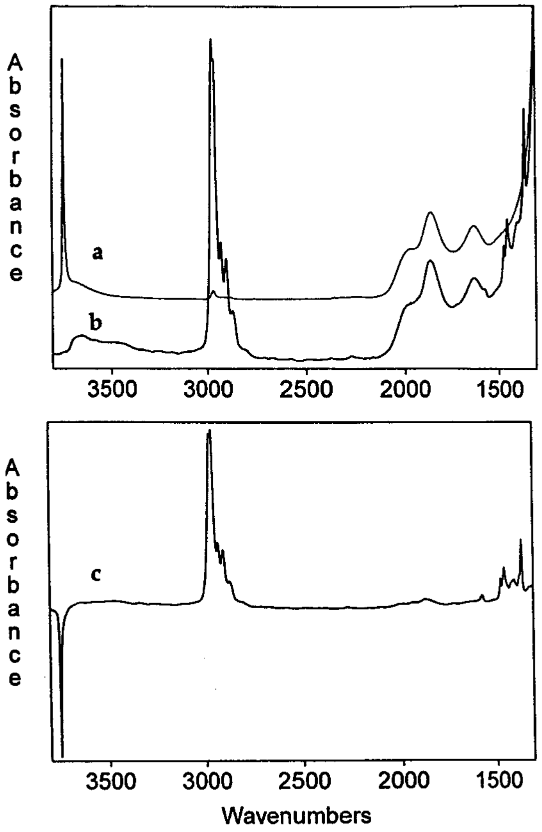

Figure 1. IR spectra of (a) self-supporting disk of silica(500); (b) after reaction with $Mo(OSiMe_3)_2(N^tBu)_2$; (c) difference spectrum (b − a). The spectrum was recorded after desorption of unreacted material and evacuation of volatile products.

Volatiles were removed by condensation with a liquid N_2 bath into a glass reactor equipped with a septum for sampling with a gastight syringe. GC analyses were performed on a Hewlett-Packard 5710A gas chromatograph with a Porasil packed column and FID detection.

The amount of chemisorbed metal was determined by quantitative extraction at the end of each experiment. Ti content was analyzed using a previously described procedure.[21] Mo content was determined by treating the modified silica sample with 4 mL of a 3:1 solution of HCl/HNO_3, heating for 30 min at 90 °C, diluting with 10 mL distilled water, and then heating for an additional 30 min. Finally, the solution was diluted to 25 mL and analyzed by ICP. (C, N) analyses were performed in air on a Perkin-Elmer 2400 Series II Elemental analyzer.

Results

Reaction of $Mo(N^tBu)_2(OSiMe_3)_2$ with Silica. When yellow $Mo(N^tBu)_2(OSiMe_3)_2$, **1**, was sublimed in vacuo at room temperature onto the surface of a silica pellet partially dehydroxylated at 500 °C, the initially colorless silica turned yellow. No products were observed in the IR spectrum of the gas phase above the pellet, and no significant amounts of volatile organic products were detected by GC.[22] After 3 h of reaction, the surface hydroxyl groups, which were visible in the IR spectrum as a sharp band at 3747 cm^{-1} (ν(SiO−H)), had disappeared, Figure 1, while new bands characteristic of

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[22] Occasionally a trace of $HOSiMe_3$ was detected by GC/FID.

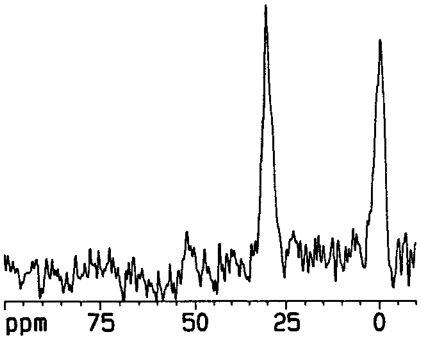

Figure 2. ^{13}C CP/MAS spectrum of silica(500) treated with $Mo(OSiMe_3)_2(N^tBu)_2$, followed by desorption of unreacted starting material and evacuation of volatile products. Spin rate is 4 kHz.

methyl stretching and deformation modes appeared.[23] After desorption of unreacted (physisorbed) starting material, elemental analysis of the solid revealed that it contained 2.1 wt % Mo, corresponding to 0.20 mmol Mo/g. This value corresponds to one-half the quantity of hydroxyl groups initially present on silica(500), 0.40 mmol/g.[2] The material also contained 3.31% C and 0.53% N, i.e., C/N/Mo = 12.6/1.7/1.0. These ratios are close to those of the starting material **1** (14/2/1), and are consistent with the absence of volatile organic products.

The ^{13}C CP/MAS solid-state NMR spectrum of the modified silica is shown in Figure 2. A weak signal at 53 ppm and a strong signal at 28 ppm are assigned to the quaternary and methyl carbons, respectively, of the *tert*-butylimido ligands, while the signal at −3 ppm is assigned to methyl carbons bound to silicon. Signal intensities in CP spectra are in general not completely quantitative; however, we expect the extent of cross polarization to different methyl carbons of similar mobility to be comparable.[24] Thus, integration of the methyl signals at 28 ppm and −3 ppm was attempted to obtain a semiquantitative estimate of their relative abundance. A ratio of 1.0/1.0 was obtained for ^{t}Bu and $SiMe_3$ methyl signals.

The ^{29}Si CP/MAS NMR spectrum of the modified silica is shown in Figure 3a. In addition to broad overlapping signals at ca. −100 ppm due to Si atoms in the lattice,[25,26] there are two new signals at 20 and 14 ppm. The signal at 20 ppm is assigned to $Me_3\mathit{Si}O$ bound to Mo, on the basis of comparison to the spectrum of **1**.[27] The signal at 14 ppm is characteristic of $Me_3\mathit{Si}O$ bound directly to the silica surface, as in $\equiv SiOSiMe_3$, **3**. Reaction of Me_3SiCl with silica gel was reported to give a ^{29}Si signal at 13 ppm assigned to **3**.[28]

To confirm the presence of two chemically distinct trimethylsiloxy environments, the modified silica was treated with excess *tert*-butyl alcohol vapor at room temperature. The Me_3SiO ligand bound to Mo is expected to exchange readily with alcohols. After 4 h of reaction with *tert*-butyl alcohol followed by evacuation of volatiles, the ^{29}Si CP/MAS NMR spectrum no longer contains the signal at 20 ppm assigned to $MoO\mathit{Si}Me_3$, whereas the signal at 14 ppm is still present, Figure 3b.

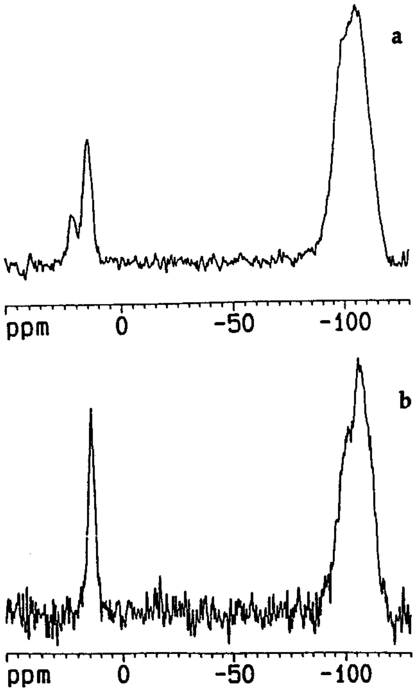

Figure 3. ^{29}Si CP/MAS spectra of silica(500) treated with (a) $Mo(OSiMe_3)_2(N^tBu)_2$, followed by desorption of unreacted starting material and evacuation of volatile products, and then treated with (b) ^{t}BuOH and then evacuated. Spin rate is 4 kHz.

The reaction of **1** with silica(200) gave rise to similar color changes, IR and NMR spectra, as well as the absence of volatile products (other than water). However the surface hydroxyls were not completely consumed, even after prolonged reaction with excess **1**. Elemental analyses of 15 independently prepared samples revealed Mo coverages in the range 2.3−2.9 wt %, corresponding to 0.36−0.41 mmol Mo/g of silica (initially containing 0.86 mmol OH/g). Elemental analyses yielded average C/N/Mo ratios of 12.5/2.0/1.0.

Reaction of $Ti(OSiMe_3)_4$ with Silica. To test whether the transfer of $SiMe_3$ groups to silica is a general feature of metallasiloxane grafting, we investigated the chemisorption of $Ti(OSiMe_3)_4$, **2**. The reaction of **2** with a silica pellet partially dehydroxylated at 500 °C gave a material containing 0.92 wt % Ti after prolonged desorption of unreacted **2**. This corresponds to 0.19 mmol Ti/g silica, which is the same metal loading as we observed for silica(500) modified by **1**.

In the IR spectrum, grafting of **2** caused the disappearance of the $\nu(SiO{-}H)$ vibration concomitant with the appearance of new bands assigned to chemisorbed $OSiMe_3$ fragments,[29] Figure 4. Two pairs of bands were observed on the modified silica: at 926/917 cm^{-1}, and 530/520 cm^{-1}. The IR spectrum of molecular **2** contains vibrations at 918 and 517 cm^{-1}, assigned to $\nu(Si{-}O)$ and

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[23] IR: 2972, 2963, 2932, 2903, 2870 cm^{-1} ($\nu(CH_3)$); 1477, 1456, 1407, 1363 cm^{-1} ($\delta(CH_3)$).

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[29] IR: 2961, 2904 cm^{-1} ($\nu(CH_3)$); 1446, 1411 cm^{-1} ($\delta(CH_3)$); 962 $\nu(O_3Si{-}OTi)$); 926, 917 cm^{-1} ($\nu(TiO{-}SiMe_3)$); 755 cm^{-1} ($\rho(CH_3)$, $\nu(SiC)$); 530, 520 cm^{-1} ($\nu(Ti{-}OSiMe_3)$).

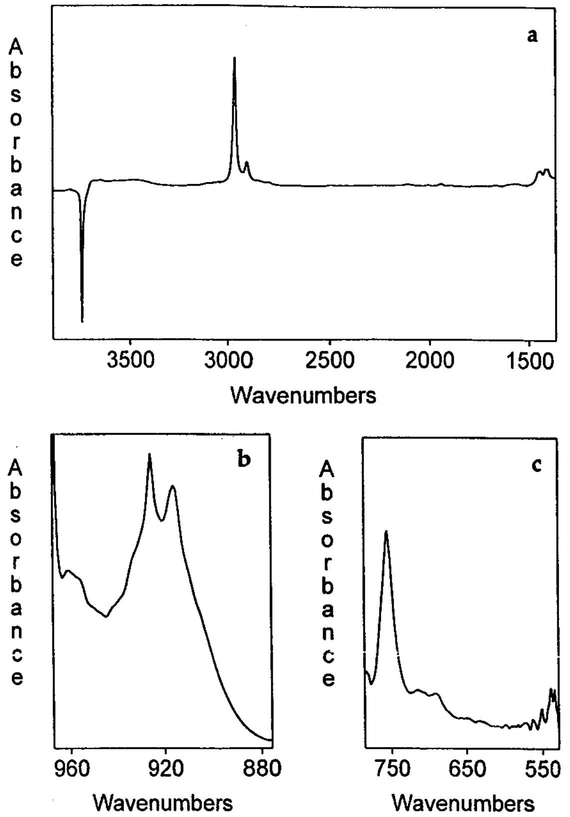

Figure 4. IR difference spectrum of a self-supporting disk of silica(500) after reaction with $Ti(OSiMe_3)_4$, in three frequency regions not obscured by the silica background spectrum. The spectrum was recorded after desorption of unreacted material and evacuation of volatile products.

ν(Ti−O), respectively.[30] The pairs of bands on the modified silica are likely associated with similar vibrational motions, for which degeneracy is reduced by the reduction in symmetry upon grafting. The band at 962 cm^{-1} is assigned to $\nu(O_3Si{-}OTi)$, which is commonly observed in Ti-substituted silicas and zeolites.[21,31,32]

The ^{29}Si CP/MAS spectrum of silica modified by **2** contains two new signals in addition to the resonances of the silica lattice, at 18 and 16 ppm, Figure 5a. The latter is assigned to chemisorbed $TiO\mathit{Si}Me_3$, by comparison to the spectrum of **2**.[33] The intensity of the 16 ppm signal decreases relative to the peak at 18 ppm upon exposure to water vapor, Figure 5b. We assign the signal at 18 ppm to **3**, such that hydrolysis causes displacement of the trimethylsiloxide ligand bound to Ti but not that bound directly to silica. Upon exposure of silica modified with **2** to $(CD_3)_2CDOD$, ~65% of the ν(C−H) intensity in the region 3050−2775 cm^{-1} was lost, while new C−D vibrations appeared. This is consistent with a partial exchange of chemisorbed trimethylsiloxide fragments.

Reaction of Me_3SiOH with Silica. Since Me_3SiOH was an expected (albeit undetected) product of both of the metallasiloxane grafting reactions described above, the reactivity of Me_3SiOH toward the silica surface was tested independently. Since this silanol is not stable, it was prepared immediately prior to use by reaction of excess $NaOSiMe_3$ with HCl vapor. The Me_3SiOH vapor was transferred via the vacuum manifold into a reactor containing a silica pellet. The observed decrease in ν(SiO−H) intensity and the appearance of CH_3 vibrations, Figure 6, confirms that chemisorption of the silanol does occur:

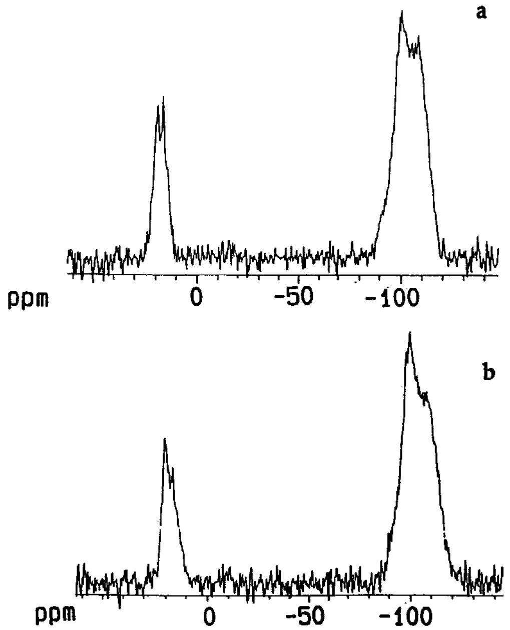

Figure 5. ^{29}Si CP/MAS spectra of silica(500) treated with (a) $Ti(OSiMe_3)_4$, followed by desorption of unreacted starting material and evacuation of volatile products, and then (b) treated with H_2O and then evacuated. Spin rate is 4 kHz.

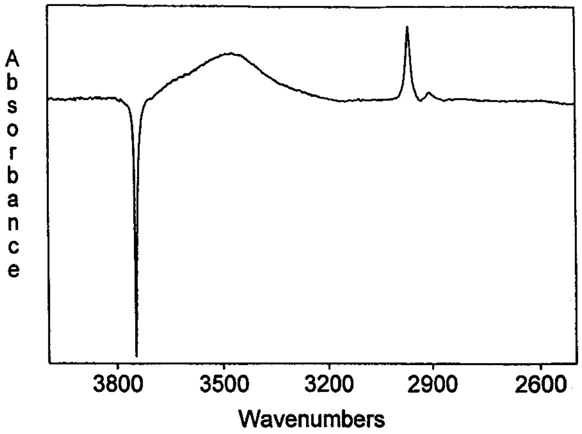

Figure 6. IR difference spectrum of a self-supporting disk of silica(500) treated with $HOSiMe_3$, followed by evacuation of unreacted material.

$$\equiv SiOH + Me_3SiOH \rightarrow \underset{\mathbf{3}}{\equiv SiOSiMe_3} + H_2O \qquad (2)$$

Hexamethyldisiloxane was also detected as a volatile product of the reaction. Its origin is presumed to be the bimolecular condensation of trimethylsilanol:

$$2HOSiMe_3 \rightarrow Me_3SiOSiMe_3 + H_2O \qquad (3)$$

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(33) Two signals were observed in the ^{29}Si spectrum of $Ti(OSiMe_3)_4$ in C_6D_6, at 6.7 and 13.5 ppm. The former is $Me_3SiOSiMe_3$, which is a byproduct of the spontaneous polymerization of $Ti(OSiMe_3)_4$. The signal at 13.5 ppm is assigned to $Ti(O\mathit{Si}Me_3)_4$ itself.

Discussion

The reactions of metal complexes with silica often occur by displacement of one or more protonated ligands, where the protons are derived from surface hydroxyl groups. Grafting, or irreversible chemisorption of metal fragments, occurs since this process is accompanied by formation of covalent Si−O-M linkages to the surface. For the metallasiloxane grafting reactions described here, the protonated ligands are not recovered. Although the material obtained by adsorption of $\mathrm{Mo(N^tBu)_2(OSiMe_3)_2}$ **1**, on silica has the same elemental analysis (C/N/Mo) as **1** as well as the same ^{13}C NMR spectrum (i.e., the ratio of ^{t}Bu to $\mathrm{SiMe_3}$ groups), irreversible chemisorption has nevertheless taken place, as evidenced by the disappearance of the IR signal for the surface hydroxyls. At maximum loading, corresponding to almost complete reaction of the surface hydroxyl groups, the Mo content of the modified silica(500) is 0.20 mmol/g, corresponding to one-half the initial quantity of surface hydroxyls (0.40 mmol/g). These results are consistent with the stoichiometry of the reaction:

$$2\equiv\mathrm{SiOH} + \underset{\mathbf{1}}{\mathrm{Mo(N^tBu)_2(OSiMe_3)_2}} \rightarrow \underset{\mathbf{3}}{\equiv\mathrm{SiOSiMe_3}} + \underset{\mathbf{4}}{\equiv\mathrm{SiOMo(N^tBu)_2(OSiMe_3)}} + \mathrm{H_2O} \quad (4)$$

Evidence for two different trimethylsiloxy environments in the modified silica is the presence of two ^{29}Si NMR signals, which respond differently to protonolysis. Thus, **3** is unreactive toward *tert*-butyl alcohol vapor at room temperature, whereas **4** undergoes ligand substitution, as shown by the disappearance of its ^{29}Si signal. Similar substitutions have been demonstrated in the reaction of $\mathrm{Mo(NAr)_2(O^tBu)_2}$ with diols[34] and calixarenes.[35] In contrast, the hydrophobic siloxane "glass bond" of $\mathrm{Me_3SiOSi}\equiv$ (**3**) is inert toward most protic reagents.

On silica(200), the observed Mo loadings correspond to reaction of 42−48% of the surface hydroxyls. According to the stoichiometry shown in eq 4, 5−15% of the silica hydroxyls therefore remain unreacted. This is consistent with the IR spectra, in which a small fraction of the $\nu(\equiv\mathrm{SiO{-}H})$ intensity remains after desorption of physisorbed **1**. The incomplete reaction of the surface hydroxyls may be a consequence of their steric inaccessibility in the presence of ~0.4 mmol/g each of **3** and **4**.

The reaction of $\mathrm{Ti(OSiMe_3)_4}$ on silica(500) results in the chemisorption of 0.19 mmol Ti/g silica, or 0.48 Ti/surface hydroxyl. The reaction stoichiometry is

$$2\equiv\mathrm{SiOH} + \underset{\mathbf{2}}{\mathrm{Ti(OSiMe_3)_4}} \rightarrow \underset{\mathbf{3}}{\equiv\mathrm{SiOSiMe_3}} + \underset{\mathbf{5}}{\equiv\mathrm{SiOTi(OSiMe_3)_3}} + \mathrm{H_2O} \quad (5)$$

Two different trimethylsiloxy environments were again observed in the ^{29}Si NMR spectrum. The sites exhibit different behavior toward excess $\mathrm{H_2O}$[36] and *tert*-butyl alcohol, with ligands on **5** undergoing protonolysis under conditions in which **3** is unreactive.

A likely grafting mechanism for the molecular metallasiloxanes begins with physisorption of **1** or **2** on a surface hydroxyl site followed by ligand protonolysis to give the anchored metal complexes **4** and **5**, accompanied by formation of trimethylsilanol:

$$\equiv\mathrm{SiOH} + \mathrm{M(OSiMe_3)}_m\mathrm{L}_n \rightarrow \equiv\mathrm{SiOM(OSiMe_3)}_{m-1}\mathrm{L}_n + \mathrm{Me_3SiOH} \quad (6)$$

Trimethylsilanol then condenses with a second silica hydroxyl group to form **3** with liberation of $\mathrm{H_2O}$, eq 2. To attain the observed grafting stoichiometries (~0.5 $\mathrm{M}/\equiv\mathrm{SiOH}$), the surface−silanol condensation reaction must be faster than the reaction of either the molecular complexes **1** and **2** or the grafted metallasiloxanes **4** and **5** with surface hydroxyl groups. In contrast, the reaction of the similar Mo alkoxide complex with silica(200) occurs with disubstitution at the metal:[21,37]

$$2\equiv\mathrm{SiOH} + \mathrm{Mo(NAr)_2(O^tBu)_2} \rightarrow (\equiv\mathrm{SiO})_2\mathrm{Mo(NAr)_2} + 2\,{}^t\mathrm{BuOH} \quad (7)$$

Release of alcohol is also obtained upon reaction of alkoxoalkylsilanes with silica hydroxyls.[38] Alcohols condense with silica hydroxyl groups to form $\equiv$SiOR and $\mathrm{H_2O}$ only at elevated temperatures (>400 K).[27] The reaction of externally generated $\mathrm{Me_3SiOH}$ with silica hydroxyls occurs at room temperature, although formation of hexamethyldisiloxane is also rapid. During grafting of **1** or **2** on silica, individual trimethylsilanol molecules are formed at the surface, where they are likely retained by hydrogen bonding. Their reaction with a proximal $\equiv$SiOH, eq 2, is thus favored relative to bimolecular formation of hexamethyldisiloxane, eq 3. Reaction of $\mathrm{Bu_3SnOSnBu_3}$ with silica(200) has been reported to yield $\equiv\mathrm{SiOSnBu_3}$, presumably via the liberation of $\mathrm{Bu_3SnOH}$.[14] However, no evidence for condensation with surface hydroxyls was obtained since the chemisorbed product of such a reaction would be spectroscopically indistinguishable from the fragment generated by direct reaction of $\mathrm{Bu_3SnOSnBu_3}$.

The local environments of **4** and **5** are therefore modified by adjacent $\mathrm{Me_3Si}$ groups adsorbed on the surface via nonhydrolyzable siloxane or "glass bonds". The different local environments of **3** derived by grafting of $\mathrm{Me_3SiCl}$,[28] **1** or **2** may account for the variability in chemical shifts (from 13 to 18 ppm) attributed to **3**. In preparing supported catalysts for reactions which are sensitive to the presence of surface protons, the presence of **3** reduces the residual hydroxyl density and renders the surface hydrophobic. The ability of metallasiloxanes to generate trialkylsilanols in situ during grafting suggests that this class of single-source precursors can be used to effect a designed dual modification of the surface.

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[36] The formation of a stoichiometric amount of water in eqs 4 and 5 apparently does not interfere with the grafting process. These reactions are performed in high vacuum conditions; presumably the water desorbs rapidly from the surface and thus is not available for protonolysis of M−O−Si or M=NR bonds. However, addition of a large excess of water does cause cleavage of these bonds.

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Conclusion

Unlike metal alkoxides, which react with surface hydroxyls of silica to produce grafted metal complexes via liberation of alcohol, metallasiloxanes give modified surfaces containing both supported metal fragments and surface organosilyl groups. Thus, the reactions of Mo(N^tBu)$_2$($OSiMe_3$)$_2$ and Ti($OSiMe_3$)$_4$ with silica produce materials which contain $\equiv SiOSiMe_3$ which is likely grafted on sites adjacent to the grafted metal complexes. The quantitative efficiency of the organosilyl derivatization results from (a) the strength of the siloxane bond formed by silanol condensation and (b) the low local concentration of silanol which disfavors bimolecular condensation reactions. This method may be useful for capping residual silica hydroxyls on supported metal catalysts, while simultaneously introducing a surface functional group to influence the catalytic properties of these new materials.

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