Metal Nanoparticle Catalysts Decorated with Metal Oxide Clusters

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Supplementary Information.

Experimental

Materials

Poly(methylhydro)siloxanes (PMHS) with trimethylsiloxy termination (average molecular weight = 1700-3200 g/mol, viscosity= 12-45 cSt, average degree of polymerization (i.e., n) estimated by NMR spectroscopy was n=38), palladium hydroxide on carbon (20 wt% loading), tetrahydrofuran (anhydrous, ≥99.9), hexanes (95%), triethylsilane (99%), and hexamethyldisilazane (99.9%) were purchased from Sigma-Aldrich Co, LLC. Celite 545 (filter aid, powder) and sodium sulfate (anhydrous, ≥99.0%) were purchased from EMD Chemicals, Inc. Ethyl ether (anhydrous, ≥99.0%) was purchased from Mallinckrodt Chemicals. Calcium sulfate ($CaSO_4$) (Drierite, without indicator, 20-40 mesh) was purchased from Acros Organics. N-methyl-aza-2,2,4-trimethylsilacyclopentane and titanium diisopropoxide (bis-2,4-pentanedionate) 75% in isopropanol were purchased from Gelest, Inc. Cab-O-Sil L-90 (amorphous, fumed silica, ≥99.8%) was purchased from Cabot Corporation.

Propane (99.999%) and custom hydrogen mixture (25.18% H_2 balanced with He) were purchased from Matheson Tri-gas. Oxygen (9.97% O_2 balanced with He) and Helium (99.999%) were purchased from Airgas, Inc.

Instruments and Analysis

For NMR measurements, the deuterated solvent was the internal reference for ^{1}H and ^{13}C, and tetramethylsilane was used as the external reference for ^{29}Si.

A Rigaku D/Max X-ray diffractometer was used for XRD analysis. The instrument was equipped with 2° divergence slit, 0.25° width (0.88 mm) receiving slit, and Ni foil filter. Several layers of Au complexes in THF were deposited and air-dried onto the ground-glass area of a quartz sample holder. Instrumental line broadening was determined to be 0.25° for Au foil at $2\Theta = 38°$. The Scherrer equation, shown below, was used to calculate the average particle size

$$d = \frac{k\lambda}{(\beta_{\text{meas}} - \beta_{\text{foil}})\cos\theta}$$

where d is particle diameter in nm, k is the dimensionless shape factor (0.9), λ is the x-ray wavelength (0.154. nm), β is the line broadening at half the maximum intensity (FWHM) in radians, and Θ is Bragg angle in radians. β_{meas} and β_{foil} are the FWHM from the sample and Au foil, respectively.

TEM images were obtained using a JEOL 2100-F transmission electron microscope with a field emission gun at 200 kV. High angle annular dark field (HAADF) STEM images had a spatial resolution of 0.2 nm. TEM samples were prepared by sonicating a suspension of 5 mg of sample in 4 mL ethanol for 10 min. After sonication, a drop was placed onto a 400 mesh copper grid with holey carbon or ultrathin carbon film (Ted Pella). The grid was then evacuated for 2 h at room temperature. ImageJ was used for particle size analysis. Particle sizes were determined by measuring the greatest pixel length between the boundaries of the particle and converting to nm.

The Brunauer-Emmet-Teller (BET) surface area was determined using the surface area and pore size distribution from equilibrium and saturation pressures measured by a Micromeritics ASAP 2010. Nitrogen was used as the analysis gas and helium as the free space gas. The amount of sample used was chosen to have a total surface area of 25 m^2 during measurements. Samples were degassed under vacuum overnight at 100 °C. The adsorption and desorption isotherms were collected in twenty data points including saturation. The surface area analysis was done with five data points.

Varian Vista MPX ICP-OES was used for inductive coupling plasma (ICP) to determine metal loading. Samples were dissolved in a mixture of concentrated hydrofluoric acid, nitric acid, and hydrochloric acid. They were then diluted to metal concentration of 5-10 ppm. Ti and Au standards were prepared from 1000 mg/L ICP standard solutions from Sigma-Aldrich Co, LLC.

Ozone was generated by corona discharge using an HG-1500 ozone generator from Ozone Solutions. The generator, with variable output control, had a capacity to generate a maximum of 1 g/h ozone at 100% set point. During catalyst treatment the set point was 10%.

A Nicolet Nexus 670 Fourier-transform infrared (FTIR) spectrometer equipped with a mercury-cadmium-telluride (MCT) detector was used for diffuse reflectance FTIR. Samples were prepared by diluting 20 mg sample into 130 mg of KBr powder. Data was collected with 4 cm^{-1} resolution and 500 scans were averaged.

X-ray photoelectron spectroscopy (XPS) was performed using a Thermo ESCALAB 250Xi equipped with an electron flood gun. The AlKα radiation (1486.6 eV) was used as an excitation source and the binding energy scale was calibrated with respect to carbon (1s).

Diffuse reflectance ultraviolet-visible (DR-UV-Vis) measurements were performed on a Perkin Elmer Lambda 1050 spectrophotometer with integration sphere. Quartz powder cells were used with barium sulfate as the background.

Preparation of Chloro(tetrahydrothiophene)gold(I)

Chloro(tetrahydrothiophene)gold(I) (Au(THT)Cl) was synthesized using the method of Uson et al.[1] $HAuCl_4(H_2O)_3$ (5 mmol, 1.97g) was dissolved in 2 mL of H_2O. While stirring, ethanol (10 ml) was added to the reaction mixture. Tetrahydrothiophene (0.56 mL) was added dropwise, forming a white precipitate. The mixture was stirred for 10 min and the precipitate was filtered and washed with three portions of 100 mL ethanol. The white powder was filtered dry and stored in a refrigerator at -30 °C.

Silylation of SiO_2 (Cab-O-Sil L-90)

Silylation of Cab-O-Sil L-90 (90 m^2/g) was prepared using a modified method of Gun’ko et al.[2] Silylated Cab-O-Sil L-90 (15 g) was placed in a 500 mL round bottom flask equipped with a glass stopcock. The contents were evacuated for 10 min. The flask was heated to 600 °C in a sand bath under evacuation for 12 h. The flask was placed in a N_2 glove box. Hexanes (390 mL), a stir bar, and 56 mmol of hexamethyldisilazane (11.7 mL, 400% excess assuming 5 $SiOH/nm^2$) were added. The mixture was stirred for 10 h. The solids were filtered, washed with 1 L of hexanes, and placed in a 500 mL Schlenk flask. The flask was evacuated for 15 min to remove residual volatiles. The flask was heated to 500 °C in sand bath under vacuum for 8 h. The powder was stored in a N_2 glove box.

Preparation of SiOH-PMHS

A 10 mL Schlenk flask equipped with a magnetic stir and rubber septum was connected to an oil bubbler. The outlet of the oil bubbler was connected to an inverted graduated cylinder filled with H_2O to measure H_2 evolution. The flask was charged with 10 mL THF, 0.64 mL PMHS (10 mmol SiH units), 0.3 mL (17 mmol) H_2O, and 30 mg of Pearlman’s catalyst (20 wt% $Pd(OH)_2/C$). H_2 evolution was monitored by the inverted graduated cylinder and was complete within 4 h. Immediately, after H_2 evolution ceased, the reaction mixture was dried by addition of 1 g of Na_2SO_4 and filtered by percolation through a narrow column packed with 15 mm Celite (top), 130 mm $CaSO_4$, 15 mm Celite, and quartz wool (bottom), followed by 80 mL ethyl ether.‡ The eluent was received by connecting the column to a 100 mL Schlenk flask that was purged with N_2. Because of the relative ease of condensation of the silanols, solvent was not removed before capping with functional groups. The ^1H, ^{13}C, and ^{29}Si NMR spectra of SiOH-PMHS is shown in Figure S1; ^1H NMR (400 MHz, $CDCl_3$) δ 0.10 ($SiCH_3$), 1.78 (THF, $OCH_2C\mathit{H}_2$), 3.61 (THF, $OC\mathit{H}_2$), 5.78 (SiOH); ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.12 (internal $SiCH_3$, $Si(OH)(\mathit{C}H_3)(OSi)_2$), 1.00 (terminal $SiCH_3$, $O\text{-}Si(\mathit{C}H_3)_3$), 25.11 (THF, $O\mathit{C}H_2$), 67.38 (THF, $OCH_2\mathit{C}H_2$) 77.00 ($\mathit{C}DCl_3$); ^{29}Si NMR (80 MHz, $CDCl_3$) δ -56.75 (internal $SiCH_3$, $\mathit{Si}(OH)(\mathit{C}H_3)(OSi)_2$), 8.02 (terminal $SiCH_3$, $O\text{-}Si(\mathit{C}H_3)_3$).

‡ Because ethyl ether reacts with molecular oxygen forming diethyl ether peroxides, a fresh bottle was opened for every use. Unknown product contamination, possibly ether peroxides, was observed in PMHS product by NMR when a bottle exposed to air for several hours was used.

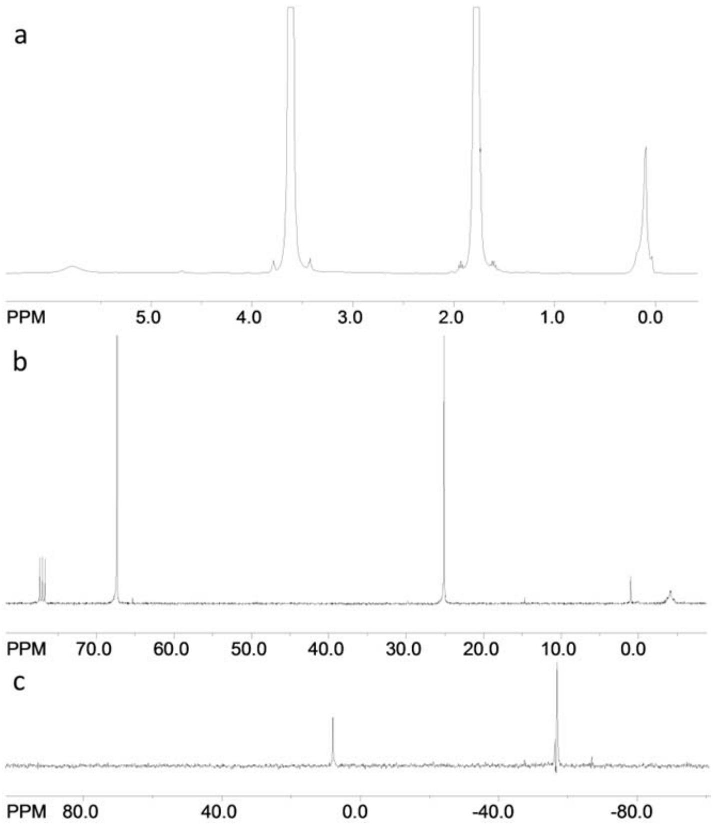

Figure S1. NMR spectra of SiOH-PMHS in THF and $CDCl_3$ (a) ^1H (b) ^{13}C (c) INEPT ^{29}Si.

Stability of SiOH-PMHS in the presence of Amine (N-methyl-aza-2,2,4-trimethylsilacyclopentane)

Silanol stability was studied by monitoring the SiOH signal by NMR after the addition of amine precursor. Partially oxidized PMHS with 2 mmol of SiOH units and 0.86 mmol of SiH units dissolved in 0.5 mL THF was mixed with 0.35 mL $CDCl_3$ and placed in an NMR tube. At time = 0 min, the amine precursor (N-methyl-aza-2,2,4-trimethylsilacyclopentane, 1 mmol, 0.18 mL) was added to the NMR tube to give a SiOH:amine ratio of 2:1 (final, after reaction ratio of SiOH:SiOSi:amine 1:1:1). Immediately after addition, an exotherm was observed suggesting that reaction had proceeded. ^1H NMR spectrum (not presented) confirmed the ring-opening and coupling of the amine precursor within 6 min. The INEPT ^{29}Si NMR spectra were obtained at different times: 17 min (64 scans), 87 min (144 scans), and 24 h (232 scans) (shown in Figure S2). The specified times are the average times between the start and end of the NMR measurements with a delayed time of 13 s and line broadening of 5. At 17 min, the formation of Si-O-Si on the PMHS was observed at -66 ppm. At -58 ppm, a SiOH (from PMHS) peak was observed with roughly the same size as the Si-O-Si pak. With 87 min of reaction time, there was still the presence of silanol, however, the size decreased in comparison to Si-O-Si. After 24 h, the SiOH completely condensed. These studies suggest that SiOH, in the presence of amine, are stable for roughly 17 min to 87 min. Ideally, the remaining SiOH groups should be utilized within this timespan. The other peaks present are $Si(H)\text{-}O\text{-}\mathit{Si}(CH_3)_3$, $Si(OR)\text{-}O\text{-}\mathit{Si}(CH_3)_3$, and Si from amine precursor bound to PMHS ($\mathit{Si}(CH_3)_2(CH_2CH(CH_3)CH_2(NH)CH_3)$-PMHS) at 7, 8, and 11 ppm, respectively.

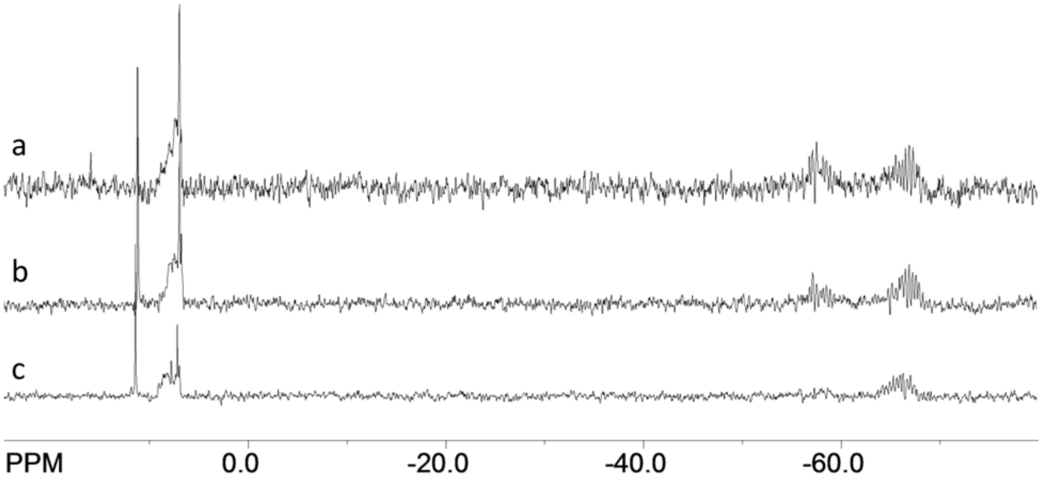

Figure S2. INEPT ^{29}Si NMR spectra of SiOH-PMHS with addition of amine precursor (2:1 of SiOH:amine) at different reaction times: (a) 17 min (64 scans) (b) 87 min (144 scans) (c) 24 h (232 scans).

Reactivity of Ti-O-^{i}Pr with SiOH-PMHS

To ensure that the Ti precursor reacted within the 17 min (as determined in the amine-SiOH stability studies), titanium diisopropoxide (bis-2,4-pentanedionate) was mixed with SiOH-PMHS. As before, partially oxidized PMHS with 2 mmol of SiOH units and 0.86 mmol of SiH units dissolved in 0.5 mL THF was mixed with 0.35 mL $CDCl_3$ and placed in an NMR tube. At time = 0 min, titanium diisopropoxide (bis-2,4-pentanedionate, 1 mmol, 0.245 mL, 75% in isopropanol) was added to the NMR tube to give a SiOH:isopropoxide ratio of 2:1 (final ratio of SiOH:SiOSi:SiOTi/isopropanol 1:1:1). At 16 min, its ^{1}H NMR spectrum (Figure S3) showed that 8% isopropoxide (4.91 ppm, (TiO)C*H*$(CH_3)_2$) remained (using pentanedionate, C*H* at 5.59 ppm, as the baseline). These results demonstrate that 92% of the isopropoxy groups reacted within 16 min, which is sufficient time after amine addition. The other peaks present are 0.07 (SiCH_3), 1.11 (isopropanol/isopropoxy, CH_3), 1.79 (THF, OCH_2CH_2), 1.96 (pentanedionate, CH_3), 3.66 (THF, OCH_2), 3.89 (isopropanol, C*H*) ppm.

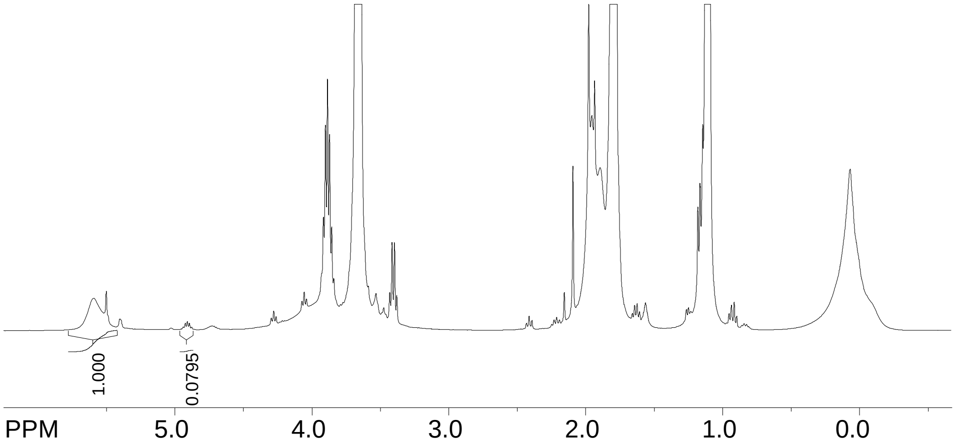

Figure S3. ^{1}H NMR spectrum of SiOH-PMHS with titanium diisopropoxide (bis-2,4-pentanedionate) (2:1 of SiOH:isopropoxide) after 16 min.

Ti-N-PMHS Samples

In order to vary the concentration of Ti at the Au periphery, two Ti-N-PMHS samples with different Ti:amine ratios were made: Ti-N-PMHS-1 for Au-$Ti_{0.7}/SiO_2$ and Ti-N-PMHS-2 for Au-$Ti_{1.5}/SiO_2$. Ti-N-PMHS-1 had 55% amine, 16% monopodal Ti, 8% bipodal Ti, 16% SiOH, and 5% SiH. Ti-N-PMHS-2 had 30% amine, 10.5% monopodal Ti, 19% bipodal Ti, 10.5% SiOH, and 30% SiH. Also, one PMHS sample, N-PMHS, was made containing no Ti for Au/SiO_2. Below are the preparation methods and characterizations.

Preparation of N-PMHS

SiOH-PMHS was freshly prepared as previously shown. SiOH (10 mmol units) in 10 mL THF and 80 mL ethyl ether was received in a 100 mL Schlenk flask equipped with a magnetic stir bar and rubber septum. With N_2 bubbling, 7.6 mmol (1.34 mL) of amine precursor (N-methyl-aza-2,2,4-trimethylsilacyclopentane) was added, initially forming a cloudy liquid. In less than 1 min, the liquid became clear. The mixture was stirred for 10 min, and solvent was removed by evacuation for 4 h. 1.38 g of a viscous clear liquid was obtained. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of N-PMHS are shown in Figure S4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.11 ($SiCH_3$), 0.41 and 0.67 ($SiCH_2CH$), 0.95 ($SiCH_2CH(CH_3)$), 1.79 ($SiCH_2CH(CH_3)CH_2$), 2.41 ($CHCH_2(NH)CH_3$ and $CH_2(NH)CH_3$), 7.27 ($CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ -2.24 (internal $SiCH_3$, $Si(OR)(CH_3)(OSi)_2$) where R = amine group, 1.11 (terminal $SiCH_3$, O-$Si(CH_3)_3$), 1.47 ($SiCH_3$ of amine), 20.98 ($SiCH_2CH(CH_3)$), 24.62 ($SiCH_2CH$), 29.05 ($SiCH_2CH(CH_3)CH_2$), 36.63 ($CH_2(NH)CH_3$), 61.71 ($CHCH_2(NH)CH_3$), 77.00 ($CDCl_3$); ^{29}Si NMR (80 MHz, $CDCl_3$) δ -66.70 (internal $SiCH_3$, $Si(OR)(CH_3)(OSi)_2$), 7.12 (terminal Si-CH_3, O-$Si(CH_3)_3$), 8.58 (Si of amine).

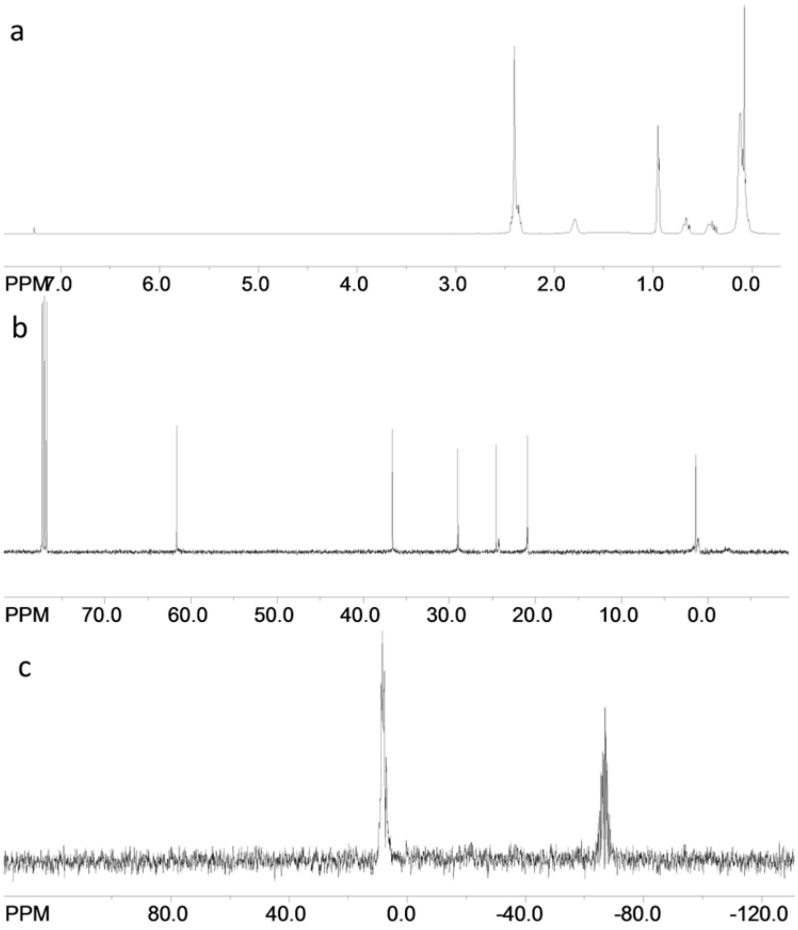

Figure S4. NMR spectra of N-PMHS in $CDCl_3$ (a) ^1H (b) ^{13}C (c) INEPT ^{29}Si.

The functional group amounts are 76% and 24% for amine and SiOH, respectively (shown in Figure S5). With chain length (n) of 38 units, the molecular weight was calculated to be 7160 g/mol.

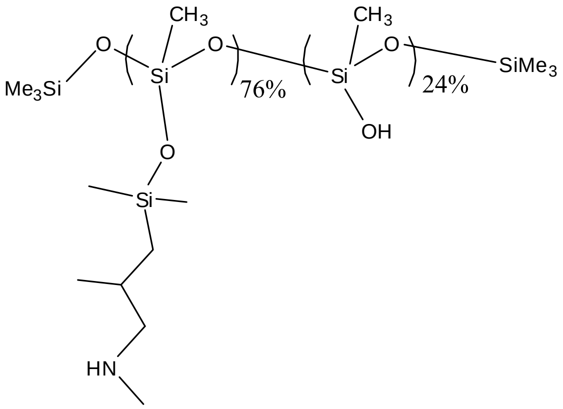

Figure S5. Structure of N-PMHS.

Preparation of Ti-N-PMHS-1

SiOH-PMHS, freshly prepared as previously shown and containing 9.5 mmol of SiOH and 0.05 mmol of SiH units in 10 mL THF, was added together with 80 mL ethyl ether into a 100 mL Schlenk flask equipped with a magnetic stir bar and rubber septum. With N_2 bubbling, 5.5 mmol (0.97 mL) of amine precursor (N-methyl-aza-2,2,4-trimethylsilacyclopentane) was added. Initially, a cloudy liquid was formed, but became clear in less than 1 min. The mixture was stirred for 5 min, and 2 mmol (0.98 mL) of Ti (titanium diisopropoxide (bis-2,4-pentanedionate), 75% in isopropanol) was added, forming a clear yellow liquid. The mixture was stirred for 2 h. Volatiles were removed by evacuation for 4 h. The resulting orange viscous liquid, 2.094 g, was stored in a N_2 glove box at -30 °C. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of Ti-N-PMHS-1 are shown in Figure S6; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.09 ($SiCH_3$), 0.42 and 0.65 (SiC*H*$_2$CH), 0.93 (SiCH$_2$CH(C*H*$_3$)), 1.16 (isopropanol/isopropoxy, C*H*$_3$), 1.76 (SiCH$_2$C*H*(CH$_3$)CH$_2$), 1.95 (pentanedionate, C*H*$_3$), 2.39 (CHC*H*$_2$(NH)CH$_3$ and CH$_2$(NH)C*H*$_3$), 4.75 (TiO)C*H*(CH$_3$)$_2$), 5.48 (pentanedionate, C*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ -2.23 (internal SiCH$_3$, Si(OR')(*C*H$_3$)(OSi)$_2$) where R' = amine or Ti group, 1.04 (terminal SiCH$_3$, O-Si(*C*H$_3$)$_3$), 1.36 (SiCH$_3$ of amine), 20.97 (SiCH$_2$CH(*C*H$_3$)), 24.54 (Si*C*H$_2$CH), 25.03 (isopropoxy, *C*H$_3$), 25.83 and 26.83 (pentanedionate, *C*H$_3$), 28.95 (SiCH$_2$*C*H(CH$_3$)CH$_2$), 36.55 (CH$_2$(NH)*C*H$_3$), 61.66 (CH*C*H$_2$(NH)CH$_3$), 77.00 ($CDCl_3$), 78.59 (isopropoxy, O*C*H(CH$_3$)$_2$), 102.52 (pentanedionate, *C*H), 187.09 and 191.16 (pentanedionate, *C*=O); ^{29}Si NMR (80 MHz, $CDCl_3$) δ -66.17 (internal SiCH$_3$, *Si*(OR')(CH$_3$)(OSi)$_2$), 7.74 (O-Si(*C*H$_3$)$_3$ and Si of amine).

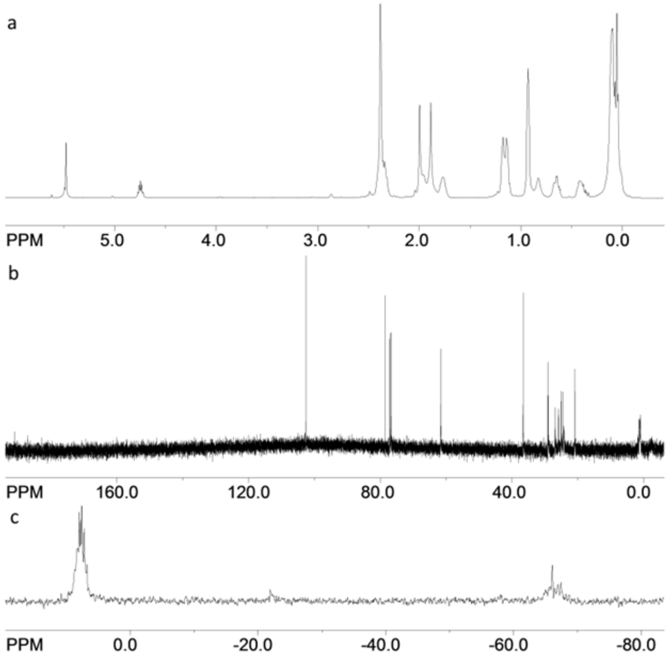

Figure S6. NMR spectra of Ti-N-PMHS-1 in $CDCl_3$ (a) ^{1}H (b) ^{13}C (c) INEPT ^{29}Si.

Under the basis of pentanedionate (6H at 1.95 ppm), integration of ^{1}H NMR spectrum shows that 40% of Ti is bound to propoxy (4.75 ppm). This suggests that Ti is 80% monopodal and 20% bipodal, under the assumption that SiOH reacts to unreacted Ti precursor before a monopodal Ti. The functional group amounts are 55%, 16%, 8%, 16%, and 5% for amine, monopodal Ti, bipodal Ti, SiOH, and SiH, respectively (shown in Figure S7). With chain length (n) of 38 units, molecular weight calculated to be 7890 g/mol.

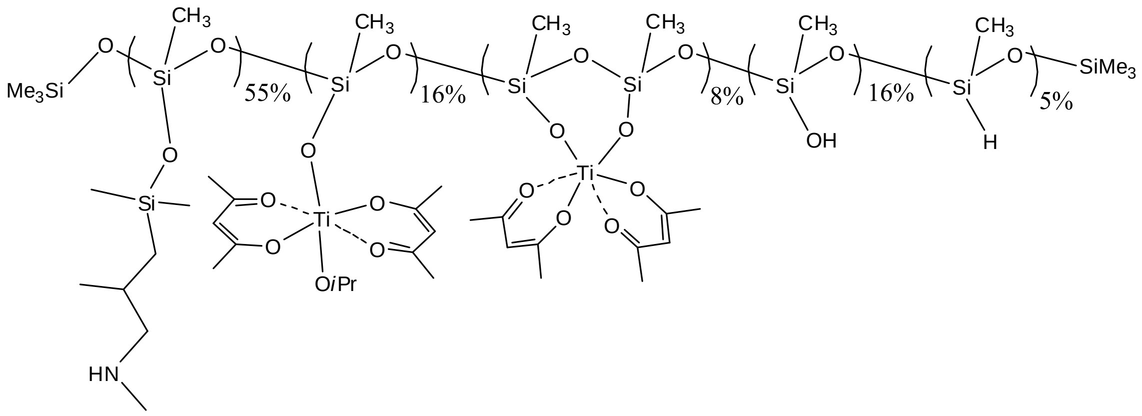

Figure S7. Structure of Ti-N-PMHS-1.

Preparation of Ti-N-PMHS-2

A freshly prepared SiOH-PMHS containing 7.0 mmol of SiOH and 3.0 mmol of SiH units in 10 mL THF and 80 mL ethyl ether were added to a 100 mL Schlenk flask equipped with a magnetic stir bar and rubber septum. With N_2 bubbling, 3 mmol (0.53 mL) of amine precursor (N-methyl-aza-2,2,4-trimethylsilacyclopentane) was added. Initially, a cloudy liquid was formed, which became clear in less than 1 min. The mixture was stirred for 5 min, and then 2 mmol (0.98 mL) of Ti (titanium diisopropoxide (bis-2,4-pentanedionate), 75% in isopropanol) was added, forming a clear yellow liquid. The mixture was stirred for 2 h. Volatiles were removed by evacuation for 4 h. The resulting orange, viscous liquid (1.514 g) was stored in a N_2 glove box at -30 °C. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of Ti-N-PMHS-2 are shown in Figure S8; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.11 ($SiCH_3$), 0.43 and 0.68 ($\mathrm{SiC}H_2\mathrm{CH}$), 0.95 ($\mathrm{SiCH_2CH(C}H_3\mathrm{))}$), 1.22 (isopropanol/isopropoxy, $\mathrm{C}H_3$), 1.81 ($\mathrm{SiCH_2C}H\mathrm{(CH_3)CH_2}$), 1.97(pentanedionate, $\mathrm{C}H_3$), 2.42 ($\mathrm{CHC}H_2\mathrm{(NH)CH_3}$ and $\mathrm{CH_2(NH)C}H_3$), 4.70 (SiH), 4.78 ($\mathrm{(TiO)C}H\mathrm{(CH_3)_2}$), 5.52 (pentanedionate, $\mathrm{C}H$); ^{13}C NMR (100 MHz, $CDCl_3$) δ -2.55 (internal $SiCH_3$, $\mathrm{Si(OR')(}C\mathrm{H_3)(OSi)_2}$) where R' = amine or Ti group, 0.97 (terminal $SiCH_3$, $\mathrm{O\text{-}Si(}C\mathrm{H_3)_3}$), 1.44 ($SiCH_3$ of amine), 20.95 ($\mathrm{SiCH_2CH(}C\mathrm{H_3))}$), 23.40-24.58 ($\mathrm{Si}C\mathrm{H_2CH}$), 25.35 (isopropoxy, $C\mathrm{H_3}$), 26.41, 26.88, and 31.87 (pentanedionate, $C\mathrm{H_3}$), 28.99 ($\mathrm{SiCH_2}C\mathrm{H(CH_3)CH_2}$), 36.52 ($\mathrm{CH_2(NH)}C\mathrm{H_3}$), 60.13 and 61.66 ($\mathrm{CH}C\mathrm{H_2(NH)CH_3}$), 77.00 ($CDCl_3$), 78.66 (isopropoxy, $\mathrm{O}C\mathrm{H(CH_3)_2}$), 60.13 and 112.62 (unbound pentanedionate, $C\mathrm{H}$), 102.32-104.6 (bound pentanedionate, $C\mathrm{H}$), 194.56 (pentanedionate, $C\mathrm{=O}$); ^{29}Si NMR (80 MHz, $CDCl_3$) δ -69.56 (internal $SiCH_3$, $Si\mathrm{(OR')(CH_3)(OSi)_2}$), 4.93 ($\mathrm{O\text{-}Si(}C\mathrm{H_3)_3}$ and Si of amine).

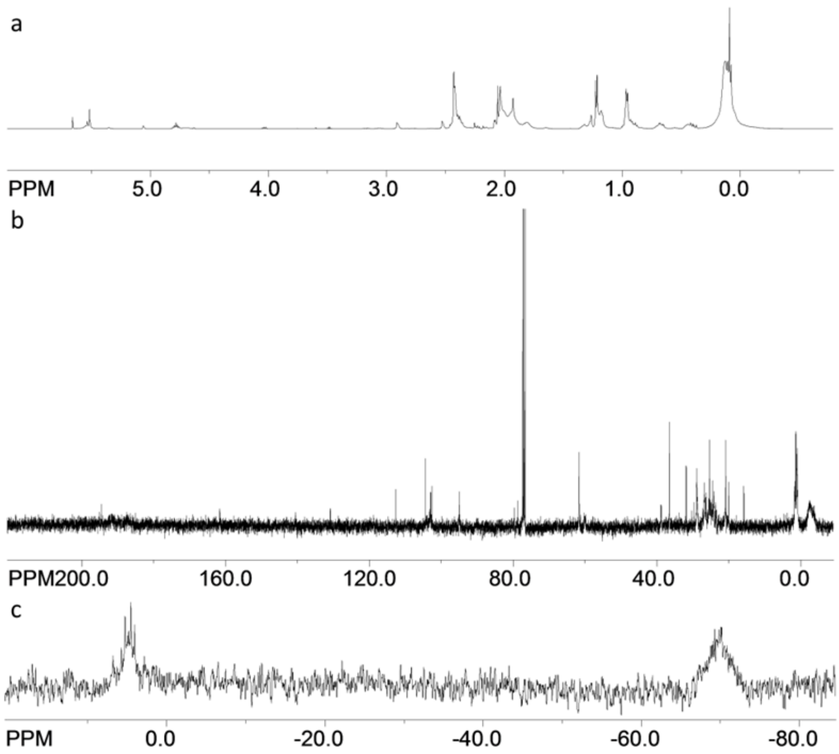

Figure S8. NMR spectra of Ti-N-PMHS-2 in $CDCl_3$ (a) ^{1}H (b) ^{13}C (c) ^{29}Si.

Based on pentanedionate (6H at 1.95 ppm), integration of the ^{1}H NMR spectrum shows that 26% of Ti is bound to propoxy (4.78 ppm). This suggests that Ti is 52% monopodal and 48% bipodal. The functional group amounts are 30%, 10.5%, 19%, 10.5%, and 30% for amine, monopodal Ti, bipodal Ti, SiOH, and SiH, respectively (shown in Figure S9). With chain length (n) of 38 units, molecular weight calculated to be 6522 g/mol.

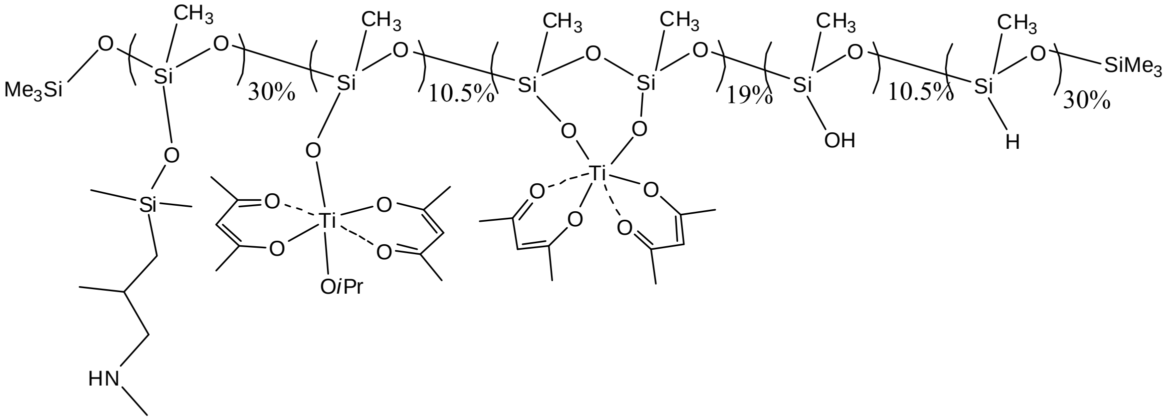

Figure S9. Structure of Ti-N-PMHS-2.

Preparation of Catalysts: Au/SiO_2, $Au\text{-}Ti_{0.7}/SiO_2$, and $Au\text{-}Ti_{1.5}/SiO_2$

Catalysts were prepared in a N_2 glove box. The following is the procedure to prepare Au/SiO_2. Au solution was prepared by dissolving 80 mg of Au(THT)Cl in 10 mL THF. In a vial, 1 mmol of amine (0.249 g of N-PMHS) was dissolved in 3.6 mL THF. Au (0.1 mmol of Au in 4 mL of Au solution) was added and stirred for 10 min. Triethylsilane (0.3 mmol, 0.048 mL) in 1.35 mL THF was added. After 5 min, the solution became a dark brown liquid. THF was added to get a total volume of 11.4 mL to be at the pore volume (5.3 mL THF/g SiO_2). The solution was added to a flask containing 2.15 g of silylated SiO_2. Being at the pore volume, the liquid completely wet the support without excess solvent. The wet brown powder was dried by evacuation for 4 h. Au-Ti/SiO_2 samples were prepared similarly but with different amounts of Ti from Ti-N-PMHS. All samples were prepared with the restrictions: amine:Au:triethylsilane molar = 10:1:3 and 0.5 wt% Au. Table S1 summarizes the preparation values.

Table S1. Summary of catalysts prepared.

	Au/SiO_2	$Au\text{-}Ti_{0.7}/SiO_2$	$Au\text{-}Ti_{1.5}/SiO_2$
PMHS type	N-PMHS	Ti-N-PMHS-1	Ti-N-PMHS-2
Amount of PMHS	0.25 g (1 mmol N)	0.36 g (0.96 mmol N)	0.86 g (1.5 mmol N)
Au(THT)Cl	0.1 mmol Au, 4.0 mL Au solution	0.096 mmol Au, 3.9 mL Au solution	0.15 mmol Au, 6.0 mL Au solution
Triethylsilane	0.3 mmol, 0.048 mL	0.29 mmol, 0.046 mL	0.45 mmol, 0.072 mL
Total THF (mL)	11.4	10.4	15.6
SiO_2 (g)	2.15	1.99	3.07

Effect of Amine:Au ratio on Particle Size

Au complex solutions with different amine:Au ratios (2, 4, 5, 10, 15) were prepared using N-PMHS as shown above (without depositing on SiO_2). Average particle sizes were determined by XRD using the Scherrer equation at $2\Theta = 38°$. The particle sizes are shown in Table S2. For the 15:1 sample, no diffraction peak was observed. This may be due to the small particle size and the highest extent of dilution by N-PMHS. TEM was used to determine the particle size for this sample. With increasing amine:Au from 2:1 to 15:1, a decrease in average particle size from 3.0 to 1.8 nm was observed. At low amine:Au ratio (2 and 4), small brown gel-like pieces precipitated within 30 min. Precipitation is likely due to Au particles behaving as a cross-linking agent for N-PMHS, forming an insoluble oligomeric network. At higher amine:Au ratios (≥5), Au complexes are stable overnight.

Table S2. Particle size determined by XRD with varying amine:Au.

Amine:Au	**Particle Size (nm)**
2:1	3.0
4:1	2.9
5:1	2.4
10:1	2.3
15:1	1.8§

§ Particle size determined by TEM.

Treatment of Catalysts

Each sample was treated in the following order: He at 130 °C, ozone at 120 °C, H_2O wash, and ozone at 150 °C.

For He treatment, 1.5 g of catalyst was placed in a fritted quartz U-tube. The U-tube was purged with He at 100 mL/min for 15 min. The U-tube was heated to 130 °C (5 °C/min) for 2h, releasing a yellow residue. ^1H and ^{13}C NMR spectra confirmed the residue was a mixture of tetrahydrothiophene, triethylsilane, and amine.

Ozone treatment at 120 °C was done to anchor the Au and Ti by partially removing ligand, before washing. 0.53 g of catalyst was placed into a fritted quartz U-tube with a wide diameter (38 mm) at the frit. The ozone penetration depth was limited to about 5 cm. Powder packed with > 5 mm thickness leads to an uneven color change and ligand removal. The U-tube was purged with O_2 at 300 mL/min for 15 min. The ozone generator was turned on (10% set point). Within minutes, the catalysts turned light gray from light brown. Ozone at room temperature was run for 15 min. The U-tube was then heated to 120 °C (0.20 °C/min), and the treatment was held for 2 h at 120 °C. Approximately 0.5 g of purple-gray powder was obtained. Partial ligand removal was confirmed by the decrease of N (1s) signal (Figure S10) in the XPS spectrum and loss of C-H band (Figure S11c) in the IR spectrum.

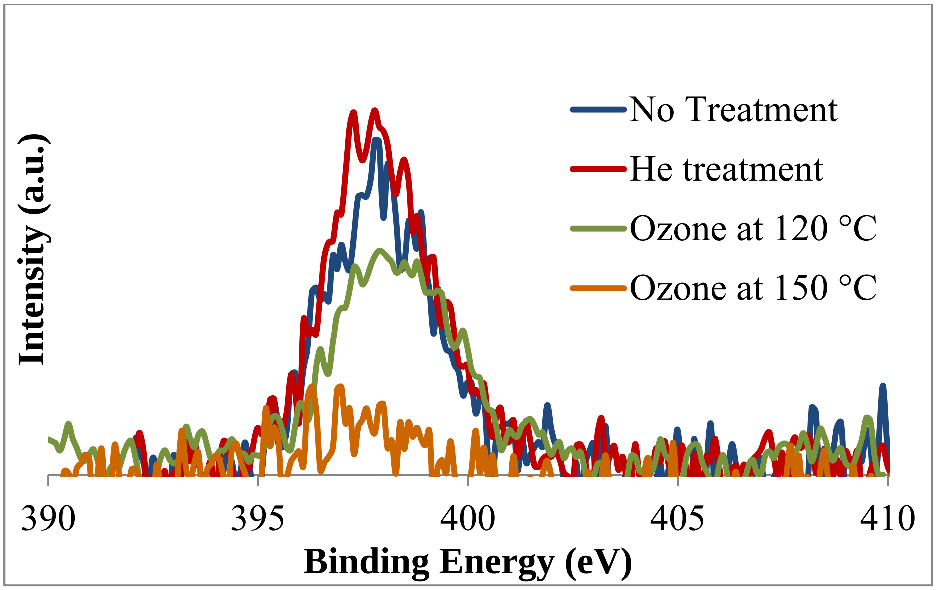

Figure S10. XPS spectra (N 1s) of Au-$Ti_{1.5}$/SiO_2 after treatments: no treatment, He at 130 °C, ozone at 120 °C, and ozone at 150 °C.

In order to remove Cl, the catalysts were washed with H_2O. One g of catalyst (previously treated with ozone treated at 120 °C) was wetted with 10 mL of ethanol, added to 100 mL H_2O at 70 °C, and the mixture was stirred for 15 min. The powder was washed with three portions of 100 mL H_2O and filtered dry. The dry powder was added to 100 mL H_2O at room temperature and stirred for 15 min. The powder was washed with three portions of 100 mL H_2O and filtered dry. No presence of Cl or S was observed by XPS before or after treatments. This is likely due to their low loadings.

After washing, the catalyst underwent a final treatment of ozone at 150 °C. Ozone treatment at 150 °C was done similarly to ozone at 120 °C except that the ramp rate was 0.15 °C/min and the final temperature was 150 °C. A light pink powder was obtained. By ozone treatment at 150 °C, a further decrease in the C-H band intensity with the loss of the shoulder (Figure S11d) and the N (1s) peak in XPS spectroscopy was observed. The majority of ligand was removed. The distinct peaks at 2910 and 2965 cm^{-1} in the IR spectrum are the C-H stretching vibrations from $SiCH_3$.

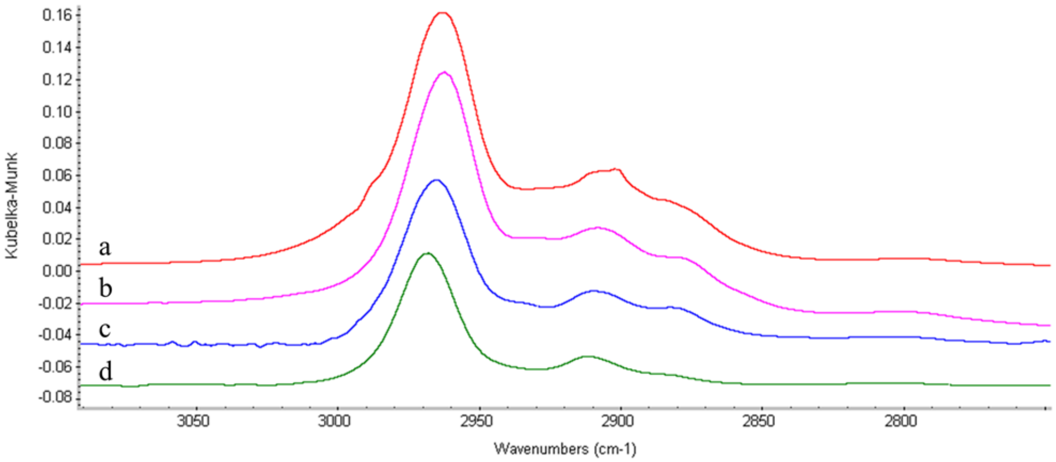

Figure S11. IR spectra of Au-$Ti_{1.5}$/SiO_2 after treatments: (a) no treatment (b) He at 130 °C (c) ozone at 120 °C (d) ozone at 150 °C.

Particle Size Analysis

After each treatment, particle size distributions were determined and the results are shown in Figures S12-S16. Table S3 summarizes the particle size distributions and the gradual increase in particle size after treatments. He treatment at 130 °C had little effect on particle size. For Au/SiO_2, there was a small increase in particle size. However, Au-$Ti_{0.7}$/SiO_2 and Au-$Ti_{1.5}$/SiO_2 showed a small decrease in average particle size, but the decrease is within analysis error. Ozone treatment at 120 °C showed an increase in particle size for Au-$Ti_{0.7}$/SiO_2 and Au-$Ti_{1.5}$/SiO_2, though very little change was observed for Au/SiO_2. After washing and treatment at 150 °C, a significant increase in particle size was observed for all samples. This is likely due to local heating by oxidation and removal of ligand, making Au more mobile.

After catalyst testing, the TEM image showed a further increase in particle size except for Au-$Ti_{1.5}$/SiO_2. All samples had converged to an average particle size of about 4 nm, which may be the stable Au particle size for propane oxidation.

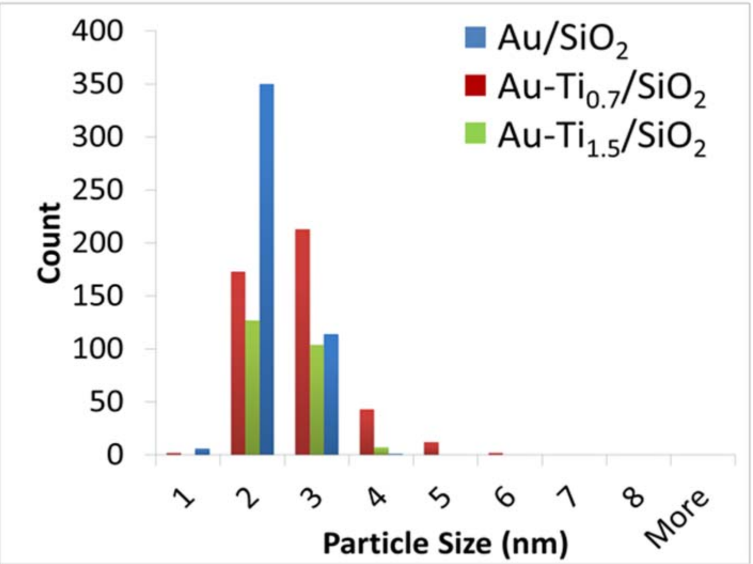

Figure S12. Au particle size distributions from TEM for samples before treatment.

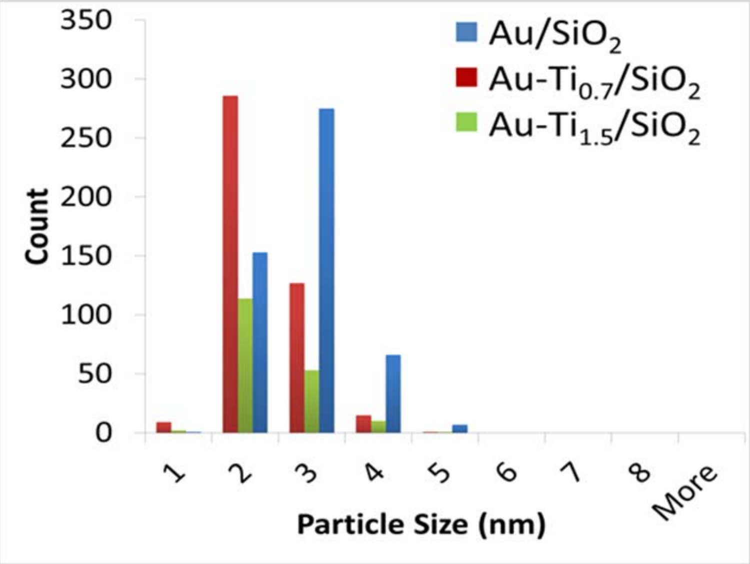

Figure S13. Au particle size distributions from TEM for samples after He treatment at 130 °C.

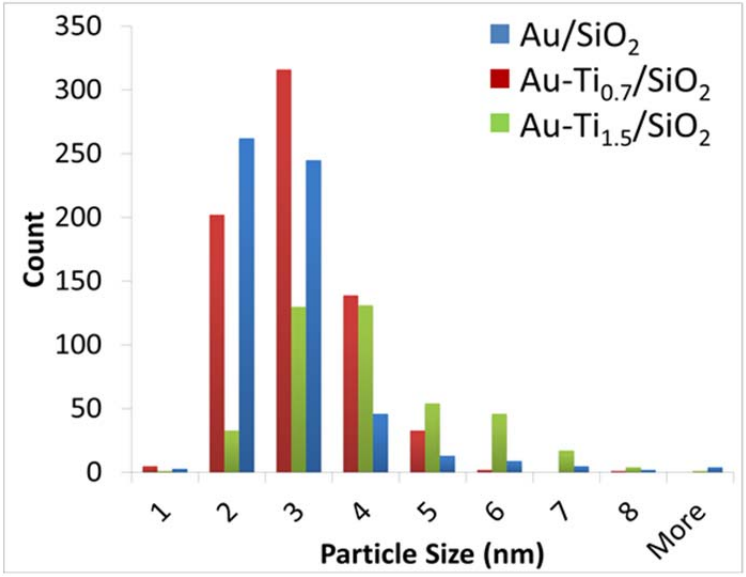

Figure S14. Au particle size distributions from TEM for samples after ozone treatment at 120 °C.

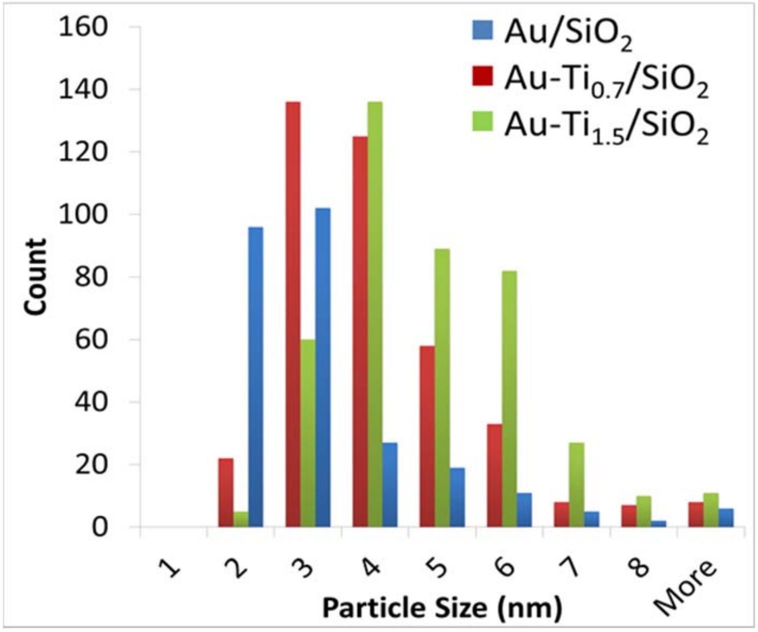

Figure S15. Au particle size distributions from TEM for samples after wash and ozone treatment at 150 °C.

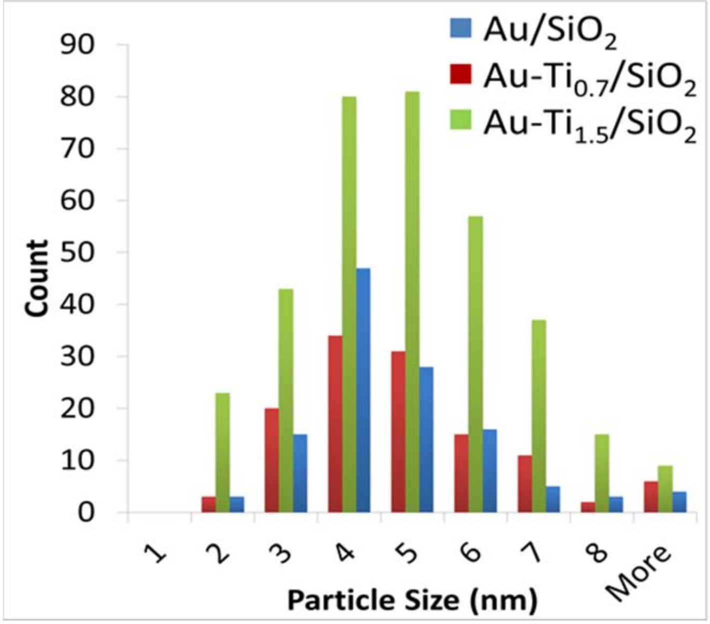

Figure S16. Au particle size distributions from TEM for samples after catalyst testing.

Table S3. Average Au particle sizes (nm) after treatments.

	Au/SiO$_2$	Au-Ti$_{0.7}$/SiO$_2$	Au-Ti$_{1.5}$/SiO$_2$
No treatment	1.8±0.4	2.3±0.7	2.0±0.5
He at 130 °C	2.4±0.6	1.8±0.5	1.9±0.6
Ozone at 120 °C	2.3±1.1	2.5±0.8	3.6±1.3
Wash and ozone at 150 °C	2.8±1.7	3.6±1.5	4.4±1.5
Post catalyst testing	4.2±1.5	4.4±1.8	4.4±1.7

XPS Analysis

The XPS results of Au 4f spectra for the three catalysts treated with ozone at 150 °C are shown in Figure S17. The binding energies were approximately 83.8 and 87.4 eV for all three samples, matching the binding energy of metallic gold. The intensities of each sample were similar in size, suggesting that the samples have similar Au loadings.

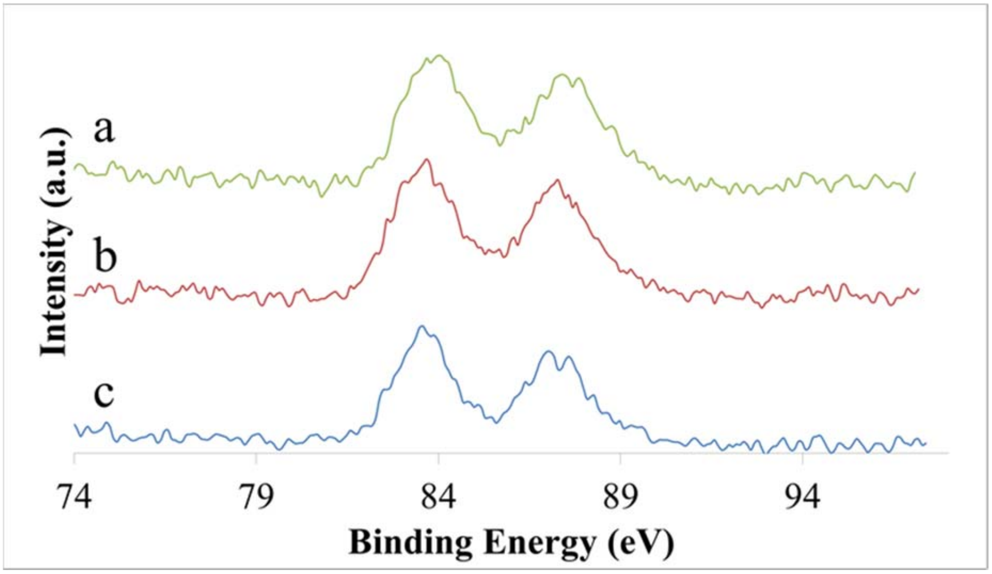

Figure S17. XPS spectra (Au 4f) of samples after ozone treatment at 150 °C: (a) Au/SiO_2 (b) Au-$Ti_{0.7}$/SiO_2 (c) Au-$Ti_{1.5}$/SiO_2.

The XPS spectra of Ti 2p spectra were also obtained as shown in Figure S18. For Au/SiO_2, no signal was detected. As expected, the intensity of Ti was higher for Au-$Ti_{1.5}$/SiO_2 compared to Au-$Ti_{0.7}$/SiO_2. The binding energies were approximately 458.8 and 464.6 eV, which corresponds to Ti^{4+}.

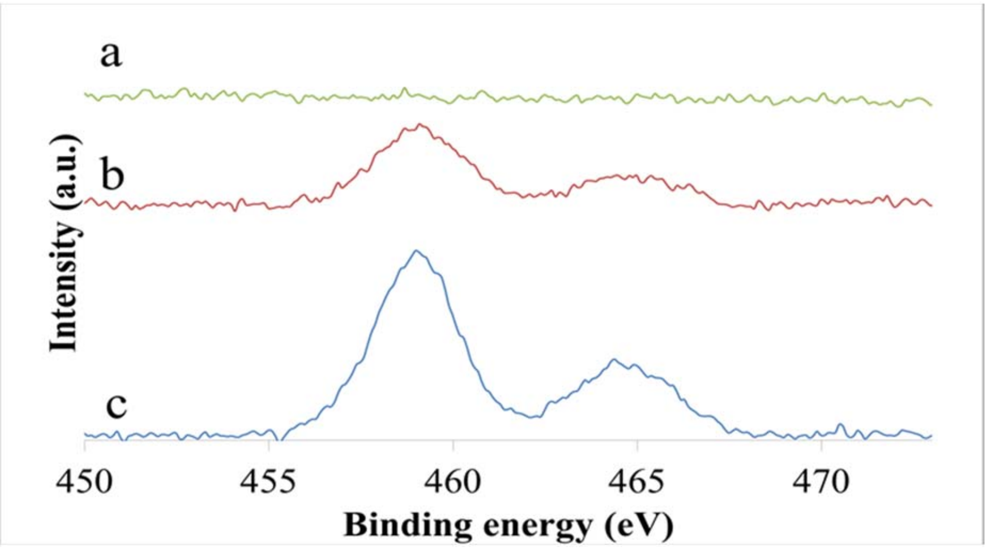

Figure S18. XPS spectra (Ti 2p) of samples after ozone treatment at 150 °C: (a) Au/SiO_2 (b) Au-$Ti_{0.7}$/SiO_2 (c) Au-$Ti_{1.5}$/SiO_2.

UV-Vis Analysis

The UV-Vis spectra (shown in Figure S19) show a peak at 250 nm and shoulder at 290 nm for Au-$Ti_{0.7}$/SiO_2 and Au-$Ti_{1.5}$/SiO_2 after ozone at 150 °C. These peaks are due to ligand to metal charge transfer (LMCT) by isolated and small Ti oligomers.[3] The absorption band of Ti is not exclusively dependent on

Ti nuclearity. Band shift is also attributed to molecular geometry and ligands. It is not clear whether the structure remained octahedral or became tetrahedral after ozone treatment or which coordination molecules (i.e. H_2O) are present. For the fraction of oligomers present, the formation is likely due to the small amount of H_2O that formed from silanol condensation during PMHS functionalization. For Au/SiO_2, the presence of these Ti peaks is absent. For all three samples, a broad absorption band due to Au at 525 nm was observed as well. All three samples had the Au band at the same position, meaning their Au particle sizes are about the same.[4]

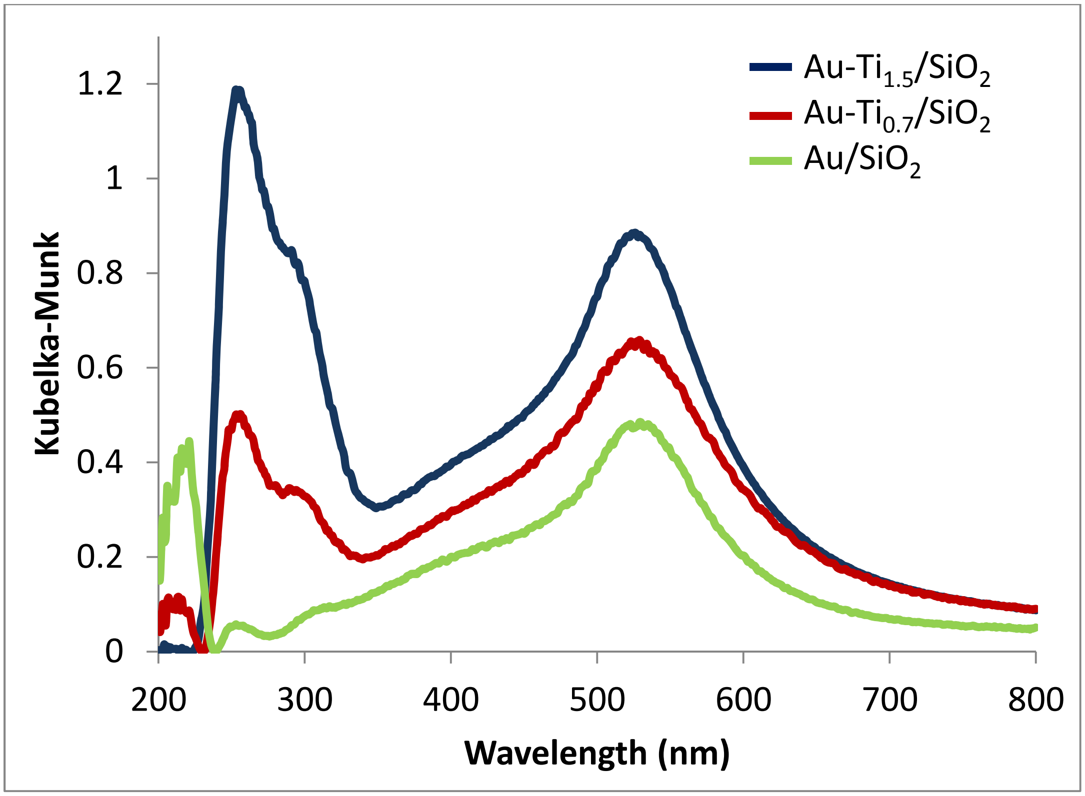

Figure S19. UV-Vis spectra of samples after ozone treatment at 150 °C.

Catalyst Testing

For catalyst testing, 350 mg of catalyst was diluted with 5 g of fine quartz powder and was subsequently placed in a quartz tubular reactor. To reduce gas-phase reactions, quartz chips were used to fill the empty volume of the reactor. A quartz thermowell was placed at the catalyst bed to monitor the local reaction temperature. The volumetric ratios for C_3H_8:O_2:H_2:He were 5:5:5:85 at 30 cm^3/min flow rate with a space-velocity of 5100 $cm^3\ h^{-1}\ g_{cat}^{-1}$. Each sample was activated at 220 °C under reaction conditions. For all samples, an activation time of 4.5 h was sufficient for CO_2 production to decrease and stabilize. The gas phase products were analyzed by on-line gas chromatography (Agilent 6890 GC with 5973 MSD) using two columns: a Porapak-Q (80/100 mesh) packed column with a TCD detector for analysis of CO_2, H_2O, propane, propene, acetaldehyde, and a Econo-cap EC-Wax capillary column with split to FID and MSD detectors for acetaldehyde, isopropanol, acetone, and other C_2-C_3 oxygenates.

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