Organosilane oxidation with half million turnover number using fibrous nanosilica supported ultrasmall nanoparticles and pseudo-single atoms of gold

Mahak Dhiman,[a] Bhagyashree Chalke[b] and Vivek Polshettiwar[a]*

[a]Nanocatalysis Laboratories (NanoCat), Department of Chemical Sciences, [b]Department of Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research (TIFR), Mumbai, India. *Email: vivekpol@tifr.res.in

Experimental Section:

Synthesis of KCC-1

KCC-1 was prepared using microwave assisted hydrothermal technique. First, cetyltrimethylammonium bromide (CTAB, 6 g, 0.016 mol) and urea (7.2 g, 0.12 mol) was stirred (1400 RPM) in water (300 mL) for 15 min. Separately, tetraethyl orthosilicate (TEOS, 30 mL, 0.14 mol) was taken in cyclohexane (300 mL) and dropwise added to above solution, which was further stirred for 15 min, followed by dropwise addition of 1-pentanol (18 mL, 0.2 mol). The resulting reaction mixture was stirred (1000 RPM) for 30 min at room temperature and then transferred in a Teflon-sealed 1 Lit microwave (MW) reactor. The reaction mixture was exposed to MW irradiation (800 W power) at 120 °C for 1 h under moderate stirring. After completion of the reaction, the mixture was allowed to cool to room temperature and the solid product formed was isolated by centrifugation, washed several times with water and ethanol, and dried at 60 °C for 12 h. The as-synthesized material was then calcined at 550 °C for 6 h in air to yield pure fibrous nano-silica (KCC-1).

Preparation of KCC-1-APTS

Grafting of APTS was carried out by refluxing 4g of calcined KCC-1 with (3-aminopropyl)triethoxysilane (4 mL, 17 mmol) in 250 mL of toluene at 80 °C for 24 h. The resulting material was washed repeatedly with toluene, and ethanol, followed by drying under vacuum at 60 °C for 12 h. The obtained material was designated as KCC-1-APTS.

Preparation of KCC-1-APTS /Au catalysts

KCC-1-APTS (500 mg) was dispersed in water (50 mL) and mixture was sonicated for 15 min followed by 10 min of vigorous stirring at room temperature. To this reaction mixture, gold(III) chloride hydrate salt of various amounts (86.2, 43, 8.6, 4.3 and 0.43 mg, taken from stock solution of $HAuCl_4$ and dissolved in 10 mL water) was added dropwise to prepare catalysts with various Au loading. Then reaction mixture was sonicated for 15 min, followed by stirring for 2 h. Freshly prepared $NaBH_4$ solution (5 mL, 1M in water) was added dropwise to this solution and was further stirred for 2 h. The resulting material was then isolated by centrifugation, thoroughly washed with water and ethanol, and dried under vacuum at 80°C for 12 h. This catalyst was named as KCC-1-APTS/Au (X%). Where X is Au loading obtained from ICP-AES analysis.

Characterization

Scanning transmission electron microscope (STEM) analysis was carried out on FEI TITAN operated at an accelerating voltage of 300 kV. For sample preparation, catalysts powder was dispersed in ethanol with assistance of sonication and a drop of solution was dropped on holey carbon coated TEM grid of 200 mesh. Excess liquid was immediately soaked with blotting paper before exposing the sample to electron beam and plasma cleaned for 5 sec. Thermogravimetric analysis (TGA) was performed using Mettler Toledo TGA/DSC2 Star instrument. X-ray diffraction patterns were recorded using Panalytical X'Pert Propowder X-ray diffractometer using Cu-Kα radiation. UV-DRS measurements were carried out using a V-770ST UV/vis/NIR spectrophotometer. The surface area was obtained using Brunauer-Emmet-Teller (BET) from N_2 physisorption data recorded using Micromeritics Flex3 analyzer. About 100 mg of each sample was degassed at 120 °C for 12 h prior to N_2 sorption analysis. XPS was acquired using a PHI 5000 VersaProbe II equipped with a monochromatic Al Kα (1486.6 eV) X-ray source and hemispherical analyzer.

Oxidation of Silanes using KCC-1-APTS/Au

KCC-1-APTS/Au (0.05%) catalyst (1 mg catalysts having 2.54E-06 mmol of Au) was placed in a 10 mL round bottom test-tube. Tetrahydrofuran (1 mL, 12.3 mmol), water (30 µL, 1.65 mmol) and silane [dimethylphenylsilane (230 µL, 1.5 mmol); triethylsilane (264 µL, 1.5 mmol,); tert-butyldimethylsilane (274 µL, 1.5 mmol); triisopropylsilane (339 µL, 1.5 mmol); 2-(Dimethylsilyl)pyridine (248 µL, 1.5 mmol); 1,2-Bis(dimethylsilyl)benzene (356 µL, 1.5 mmol); benzyldimethylsilane (261 µL, 1.5 mmol) or tri-phenylsilane (430 mg, 1.5 mmol)] was added to the reaction tube and the reaction mixture was vigorously stirred at 45 °C. Reaction was monitored by GC for 22 hours by taking aliquots at regular intervals of time and the products were determined by GC-MS analysis.

Alcoholysis of Silanes using KCC-1-APTS/Au

KCC-1-APTS/Au (0.05%) catalyst (1 mg catalysts having 2.54E-06 mmol of Au) was placed in a 10 mL round bottom test-tube. Tetrahydrofuran (1 mL), dimethylphenylsilane (230 µL, 1.5 mmol) and alcohol [1-hexanol (168 µL, 1.5 mmol); 1-propanol (124 µL, 1.5 mmol); furfuryl alcohol (162 µL, 1.5 mmol); 4-isopropylbenzylalcohol (247 µL, 1.5 mmol) or 4-penten-1-ol (171 µL, 1.5 mmol)] was added, and the reaction mixture was vigorously stirred at 45 °C. Reaction was monitored for 24 hours by GC and the products were determined by GC-MS analysis.

Hydrosilylation Reaction using KCC-1-APTS/Au

KCC-1-APTS/Au (0.05%) catalyst (1 mg catalysts having 2.54E-06 mmol of Au) was placed in a 10 mL round bottom test-tube. Tetrahydrofuran (1 mL), dimethylphenylsilane (153 µL, 1 mmol) and aldehyde [*p*-anisaldehyde (408 µL, 3 mmol); cuminaldehyde (453 µL, 3 mmol); 4-chlorobenzaldehyde (421 µL, 3 mmol) or 4-fluorobenzaldehyde (372 µL, 3 mmol)] was added and purged with argon gas. The reaction mixture was vigorously stirred at 75 °C. Reaction was monitored for 24 hours by GC and the products were determined by GC-MS analysis.

Procedure for Catalysts Recycling Study

KCC-1-APTS/Au (0.05%) catalyst (1 mg catalysts having 2.54E-06 mmol of Au) was placed in a 10 mL round bottom test-tube. Tetrahydrofuran (1 mL, 12.3 mmol), dimethylphenylsilane (230 µL, 1.5 mmol) and water (30 µL, 1.65 mmol) were added, and the reaction mixture was vigorously stirred at 45 °C for 22 hours. After completion of the reaction, reaction was cooled to room temperature and reaction mixture was centrifuged for 30 minutes at 14000 rpm. The catalyst was separated from the reaction mixture, washed with tetrahydrofuran two times and then re-used for the subsequent cycles. This was repeated up to 10 cycles. Some loss in catalyst amount was observed during the centrifugation and washing step.

Procedure for Hot Filtration Test

Hot filtration test was conducted to confirm that the nanocatalyst was indeed stable and leach proof. KCC-1-APTS/Au (0.05%) catalyst (1 mg catalysts having 2.54E-06 mmol of Au) was placed in a 10 mL round bottom test-tube. Tetrahydrofuran (1 mL, 12.3 mmol), dimethylphenylsilane (230 µL, 1.5 mmol) and water (30 µL, 1.65 mmol) were taken and stirred at 45 °C for 12 hours to reach around 55 % conversion. The catalyst was then quickly removed from the hot reaction mixture, and the filtrate was monitored for further progress of the reaction by GC. A parallel reaction without catalyst removal was also carried out as a control.

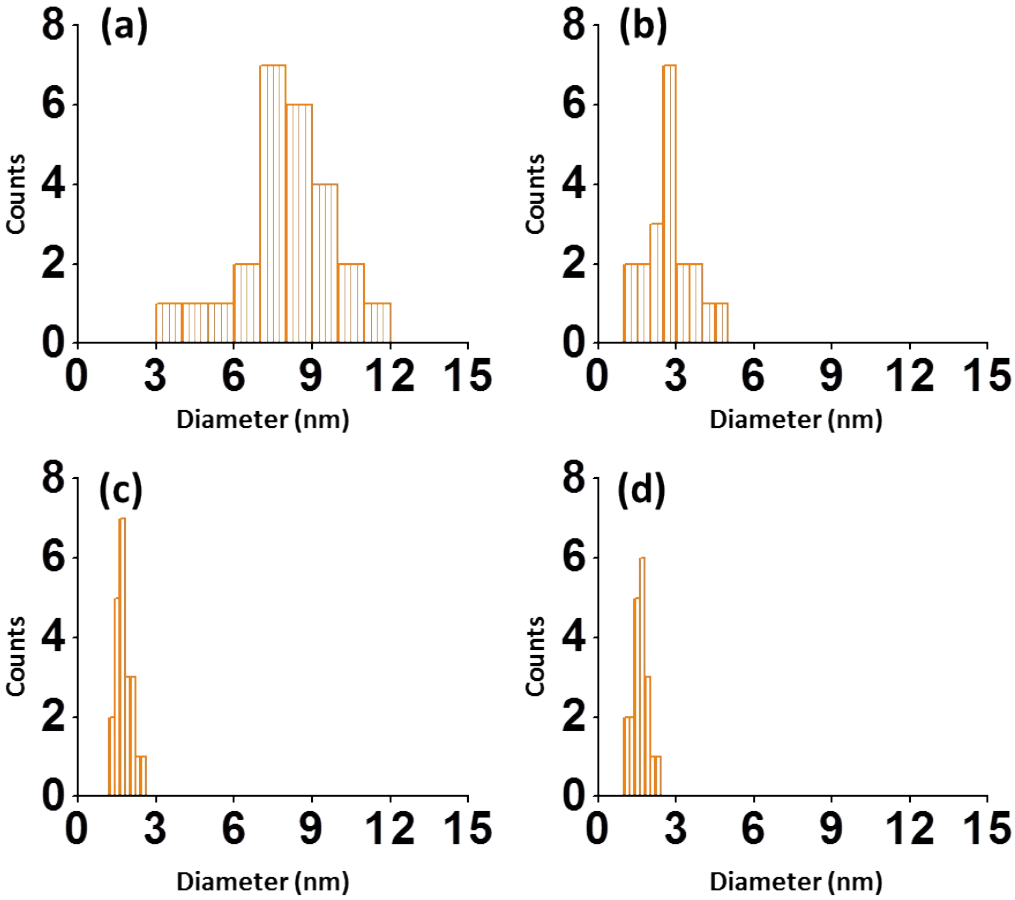


Figure S1. Particle size distribution of (a) KCC-1-APTS/Au (7.5%), (b) KCC-1-APTS/Au (4.1%), (c) KCC-1-APTS/Au (0.9%), (d) KCC-1-APTS/Au (0.7%). *KCC-1-APTS/Au (0.05%) catalyst showed mixture of ultra-small Au nanoparticles and substantial number of pseudo single atoms of Au. Therefore, depiction of particle size distribution is not possible.*

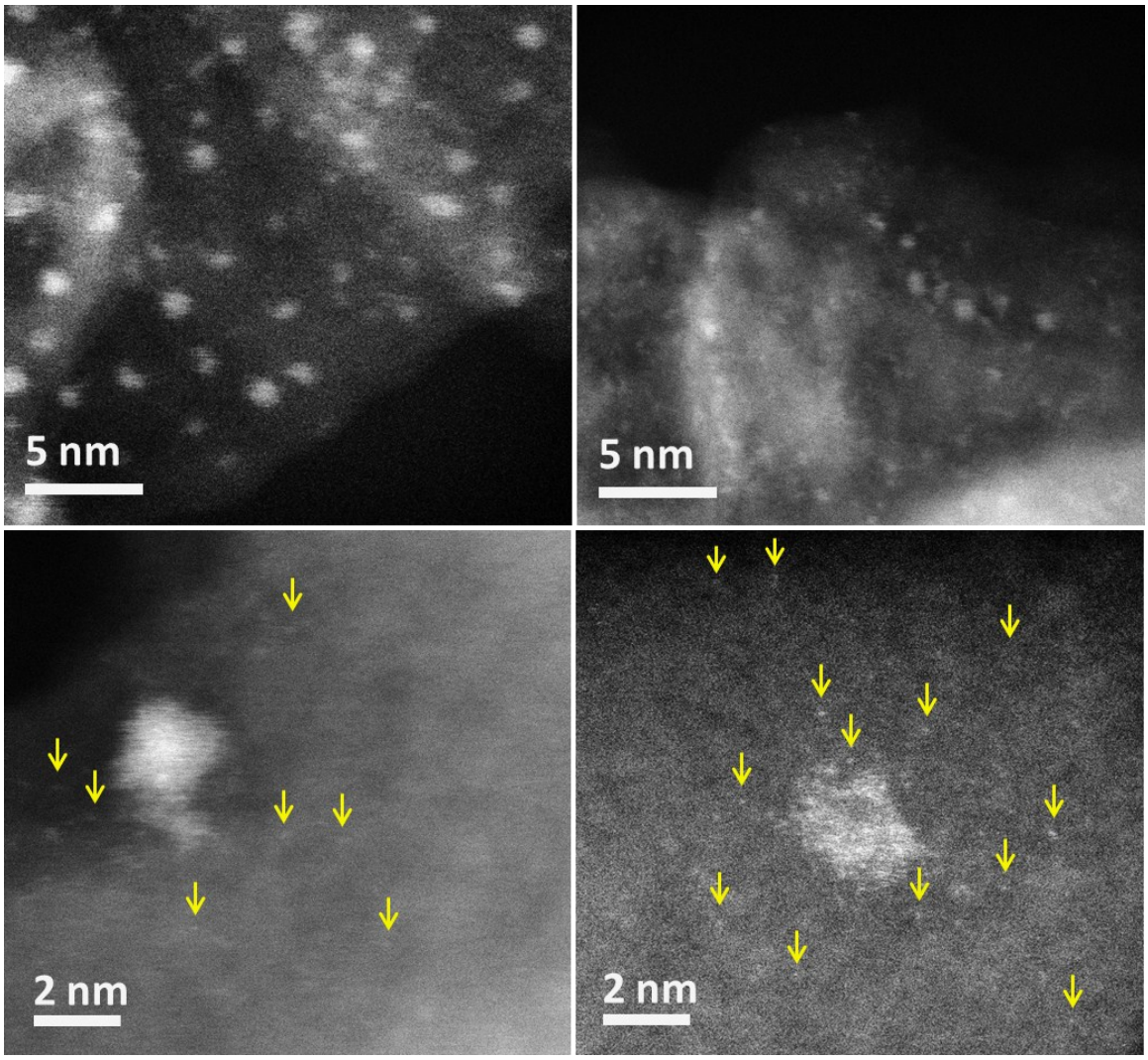
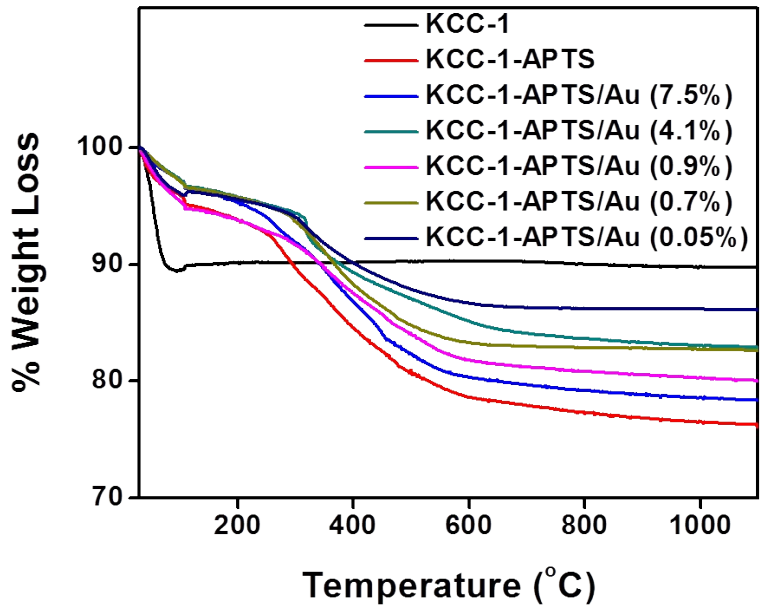


Figure S2. HR-STEM Images of KCC-1-APTS/Au (0.05%). *Arrows indicate sub-nanometer sized nanoparticles (pseudo-single atoms). Poor contrast was due to instability of pseudo-single atoms of Au supported on non-conducting silica, in presence of electron beam. All similar reported catalysts were on conducting support, hence they able to achieve better imaging. However, in our case, due to inherent non-conducting behavior of silica, we were not able to obtain better images even after several attempts in Titan TEM using HRTEM and STEM mode.*



Catalysts	Weight Loss (%)
KCC-1	0.2
KCC-1-APTS	19
KCC-1-APTS/Au (7.5%)	18
KCC-1-APTS/Au (4.1%)	14
KCC-1-APTS/Au (0.9%)	15
KCC-1-APTS/Au (0.7%)	14
KCC-1-APTS/Au (0.05%)	12

Figure S3. Thermogravimetric profile of various KCC-1-APTS/Au catalysts. *After minor weight loss due to adsorbed moisture, the major weight loss around 300 ^{0}C was due to loss of APTS molecules from KCC-1 surface.*

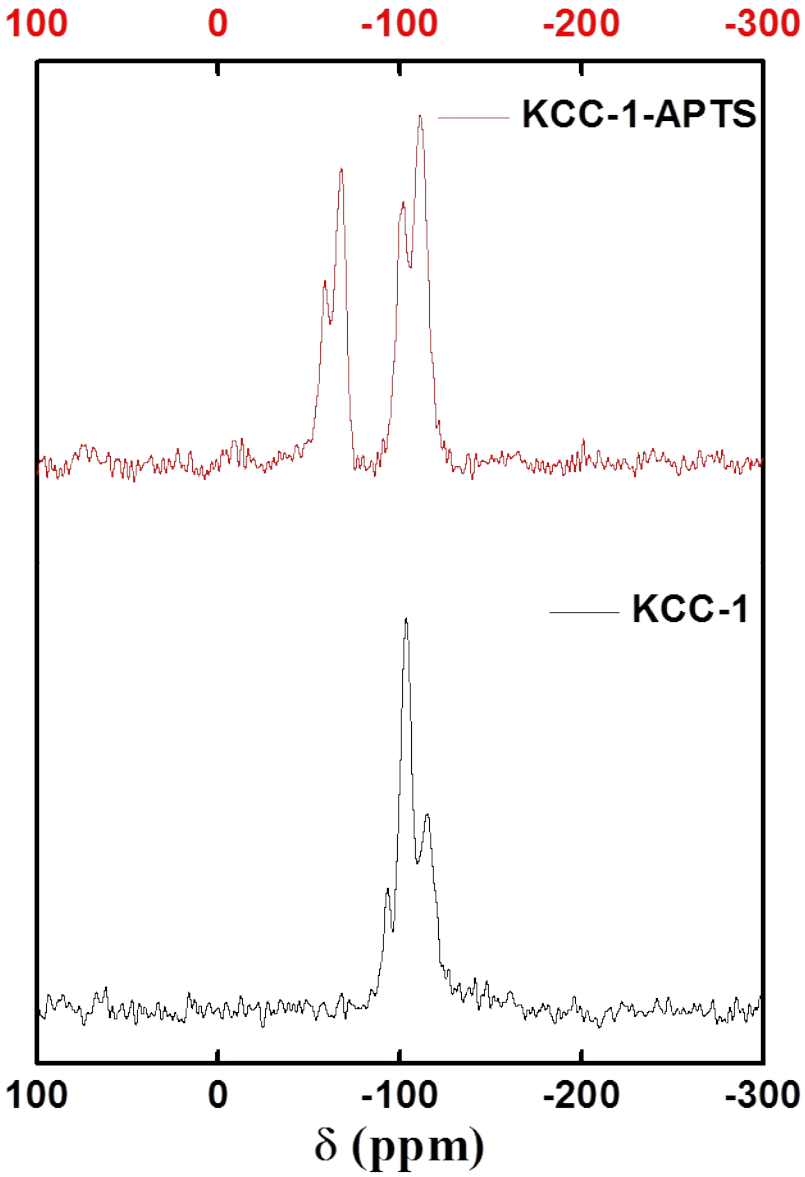


Figure S4. ^{29}Si CP-MAS NMR spectrum of KCC-1 and KCC-1-APTS. *In KCC-1, the peaks at approximately −110 and −100 ppm, correspond to Q^4 sites (SiO_4) and Q^3 (SiO_3-OH) sites respectively. In KCC-1-APTS, additional peaks centered at approximately −67.59 and −58.59 ppm belongs to T^3 {(C-Si(OSi)$_3$} and T^2 {(C-Si(OSi)$_2$OH} sites respectively, confirming the covalent functionalization of 3-APTS molecules on the surfaces of KCC-1.*

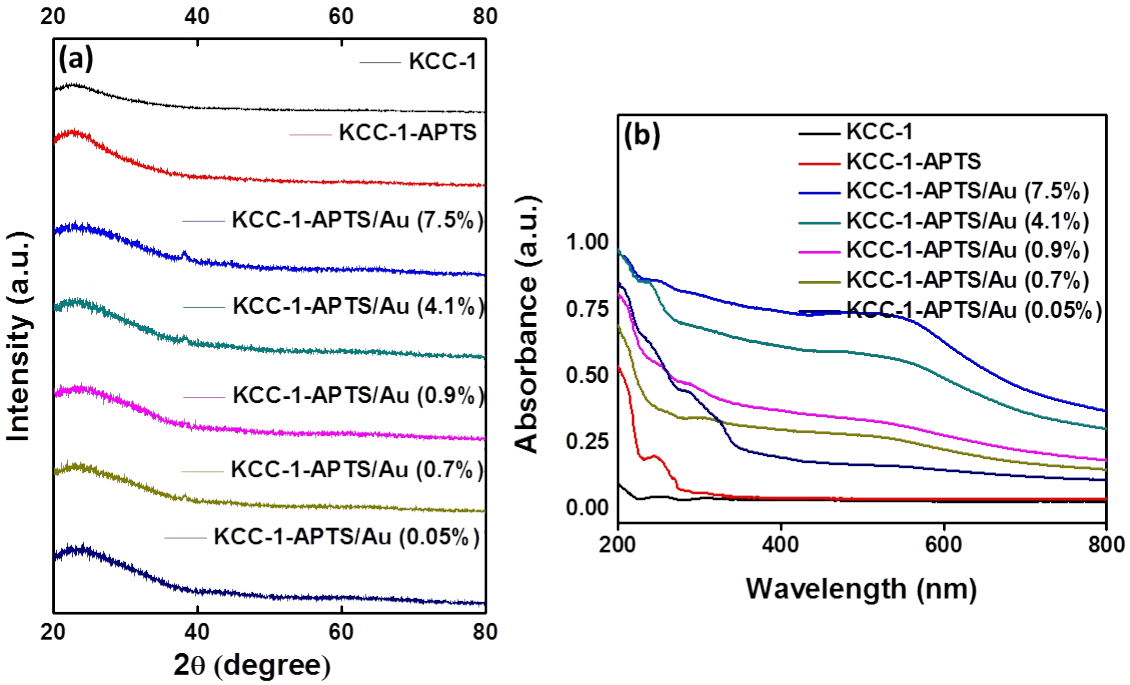


Figure S5. (a) PXRD pattern, (b) UV-Vis diffuse reflectance spectra, of KCC-1, KCC-1-APTS, and various KCC-1-APTS/Au catalysts. *PXRD patterns showed a broad hump at 25° which is characteristic of the amorphous nature of silica. Small-sized Au NPs supported on silica did not provided coherent diffraction, thus leading to weak signal at 38° for (111) plane of metallic Au. The electric field of incident light induces coherent oscillation of Au NPs conduction band electrons with respective to the positively charged Au core, known as surface plasmon resonance (SPR). SPR wavelength was around 541 nm for KCC-1-APTS/Au (7.5%), which was shifted to 516 nm for KCC-1-APTS/Au (4.1%), to 512 nm for KCC-1-APTS/Au (0.9 and 0.7 %), and not detectable in case of KCC-1-APTS/Au (0.05%). This shift in SPR confirms the reduction in Au NPs particle size from 7.5% to 0.05% catalysts, as observed in TEM. Weak SPR in KCC-1-APTS/Au (0.05%) confirms the presence of ultrasmall of pseudo single atoms of Au*

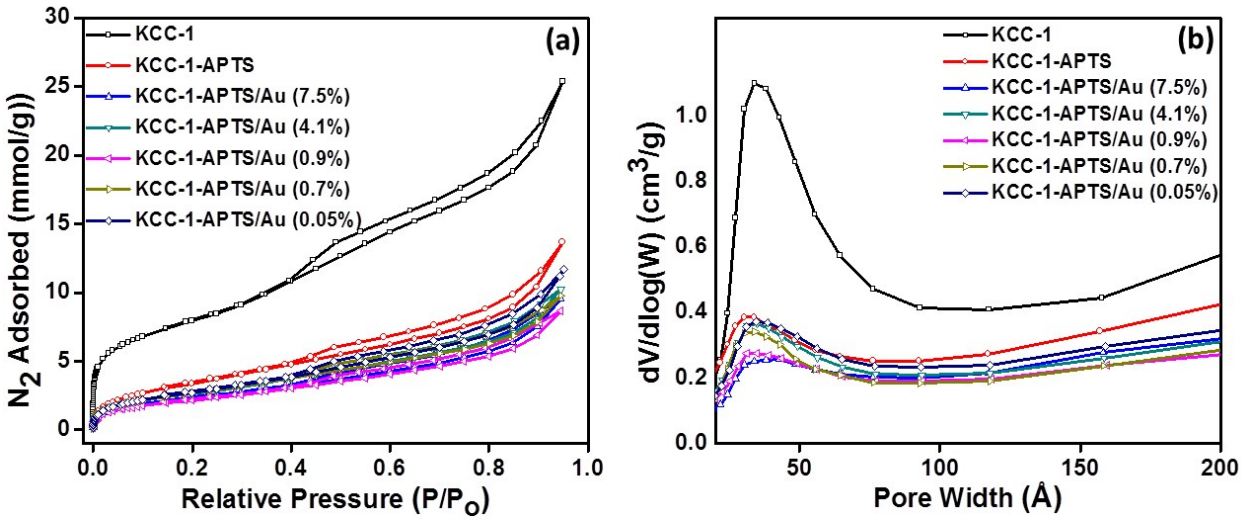


Figure S6. (a) Nitrogen adsorption–desorption isotherm, (b) pore size distribution, of KCC-1, KCC-1-APTS, and various KCC-1-APTS/Au catalysts.

Table S1. Textural properties of the KCC-1-APTS/Au catalysts.

Catalyst	BET Surface Area (m^2/g)	BJH Pore Volume (cm^3/g)	Au Loading (Wt. %)
KCC-1	638	0.83	0
KCC-1-APTS	286	0.47	0
KCC-1-APTS/Au (7.5%)	192	0.33	7.5
KCC-1-APTS/Au (4.1%)	224	0.36	4.1
KCC-1-APTS/Au (0.9%)	184	0.31	0.9
KCC-1-APTS/Au (0.7%)	215	0.33	0.7
KCC-1-APTS/Au (0.05%)	232	0.30	0.05

Measurement standard errors, Surface area ± 5 %, Pore volume ± 0.01.

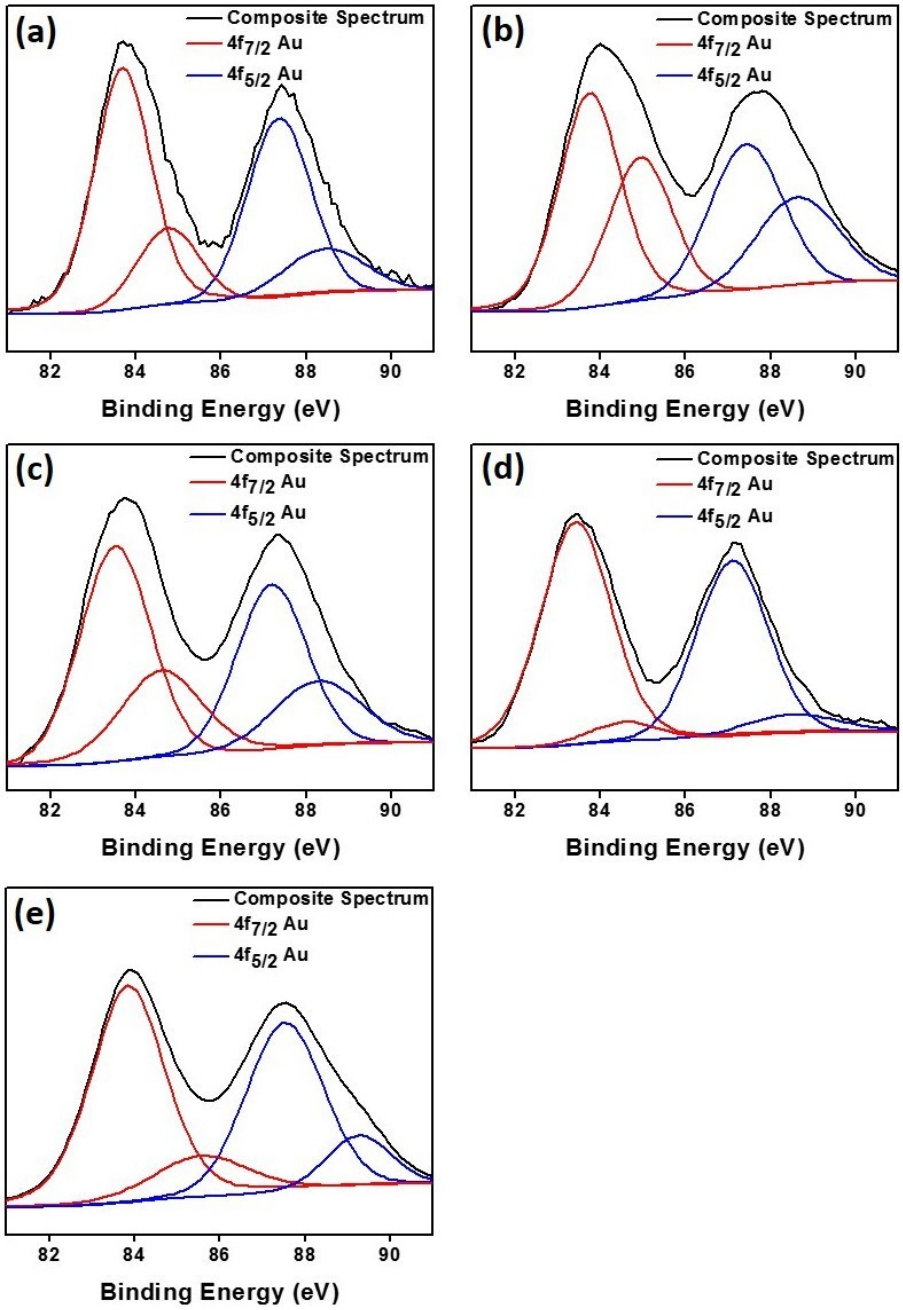


Figure S7. Au 4f XPS spectra of (a) KCC-1-APTS/Au (7.5%), (b) KCC-1-APTS/Au (4.1%), (c) KCC-1-APTS/Au (0.9%), (d) KCC-1-APTS/Au (0.7%) and (e) KCC-1-APTS/Au (0.05%). *XPS spectra of KCC-1-APTS/Au catalysts showed broad peaks in Au 4f region, indicating the presence of* $Au^{\delta+}$ *with different oxidation state in addition to* Au^{o}*. Au* $4f_{7/2}$ *was de-convoluted into two peaks, first at 83.71 eV for* Au^{o} *and 84.77 eV for* $Au^{\delta+}$*. Au* $4f_{5/2}$ *was also de-convoluted into two peaks, first at 87.37 eV for* Au^{o} *and 88.48 eV for* $Au^{\delta+}$*. The presence of* $Au^{\delta+}$ *species was observed in all synthesized catalyst with varied concentrations.*

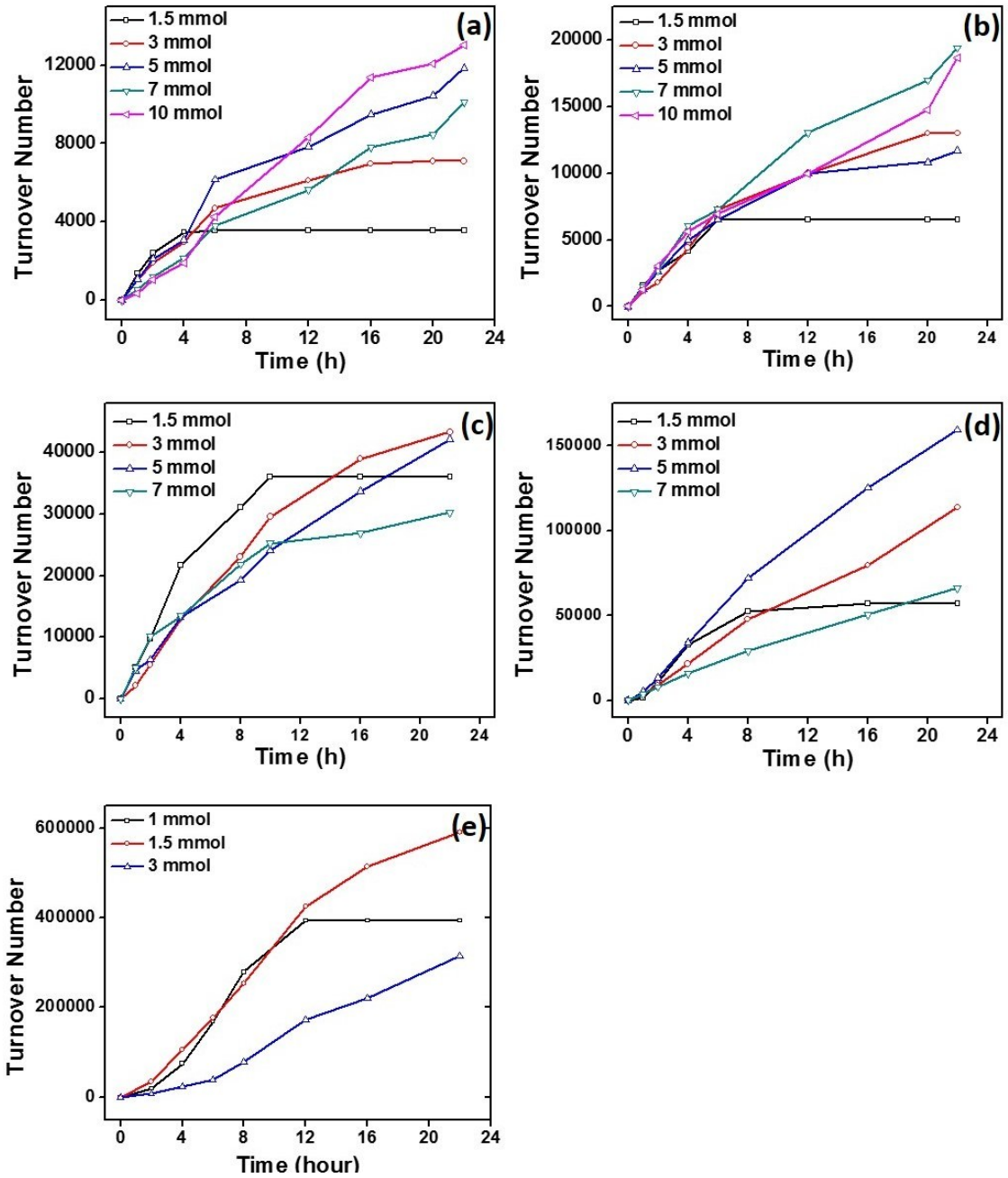


Figure S8. Oxidation of dimethylphenylsilane (DMPS) to dimethylphenylsilanol using a) KCC-1-APTS/Au (7.5%), (b) KCC-1-APTS/Au (4.1%), (c) KCC-1-APTS/Au (0.9%), (d) KCC-1-APTS/Au (0.7%) and (e) KCC-1-APTS/Au (0.05%). *Reaction conditions: DMPS (mmol as mentioned in the above figure), catalyst (1 mg), tetrahydrofuran (1 mL), water (30µL) and reaction temperature 45 ^{o}C.*

Table S2. Optimization of amount of catalyst, reaction temperature and solvents for dimethylphenylsilane oxidation using KCC-1-APTS/Au (0.05%) catalyst.

S.N.	Solvent	Amt. of Catalyst (mg)	Reaction Temp. (^oC)	Reaction Time (h)	Conversion (%)	Selectivity (%)	TON
1	THF-H_2O	1	45	22	100	100	591000
2	THF-H_2O	5	45	22	100	100	118000
3	THF-H_2O	10	45	22	100	100	59100
4	THF-H_2O	1	25	22	60	100	355000
5	THF-H_2O	1	60	22	63	100	372000
6	THF	1	45	22	5	100	19685
7	H_2O	1	45	22	38	100	224580

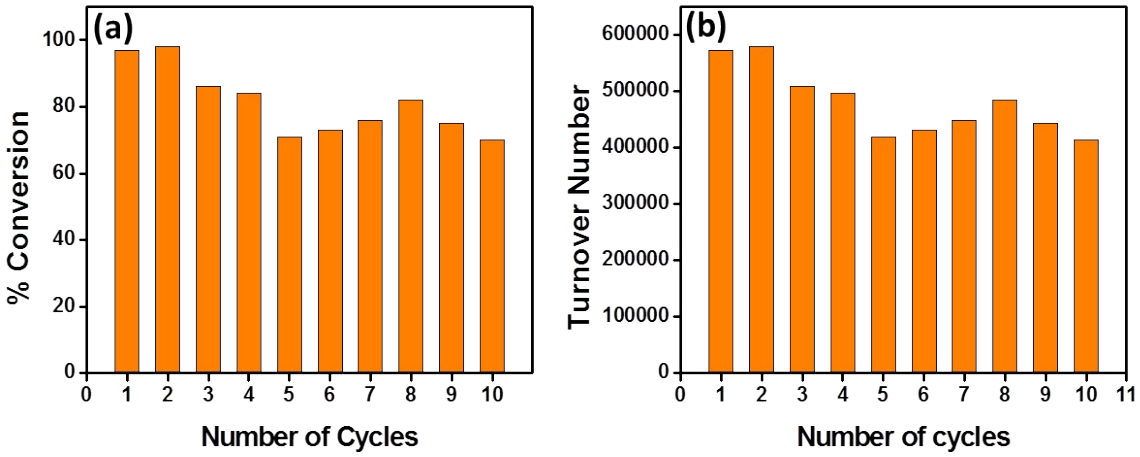


Figure S9. Recycling study of (a) % conversion, (b) turnover number with number of cycles. *The catalyst was nearly stable up to 10 cycles with slight reduction in TON, possibly due to the loss of some amount of catalyst during each cycle.*

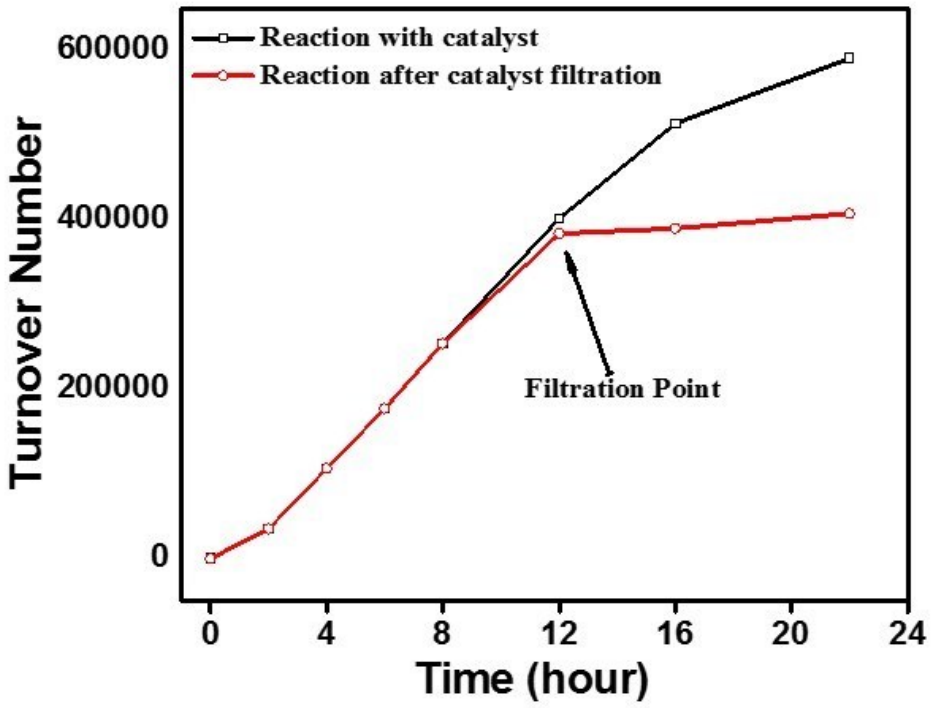


Figure S10. The hot filtration test for dimethylphenylsilane oxidation by KCC-1-APTS/Au (0.05%). *Filtration point is the time point when catalyst was filtered off from the hot reaction mixture. The supernatant was monitored for further progress of the reaction by GC-MS. A parallel reaction without catalyst filtration was also carried out as control.*