

Organosilane oxidation by water catalyzed by large gold nanoparticles in a membrane reactor

Vitaly Gitis,^{a,b*} Rolf Beerthuis,^a N. Raveendran Shiju,^{a*} Gadi Rothenberg^a

^a Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098XH Amsterdam, The Netherlands.

^b Unit of Environmental Engineering, Ben-Gurion University of the Negev, PO Box 653, Beer-Sheva 84105, Israel.

Experimental procedures

a. Synthesis of gold nanoparticles

Monodispersed gold aquasols of varying sizes were prepared using the citric acid/tannic acid method. A detailed description of this procedure is published elsewhere.¹ In this method, hydrogen tetrachloroaurate was reduced with sodium citrate and tannic acid. For instance, 4.0 ml of a 1% solution of trisodium citrate and 5.0 ml of tannic acid were added to 40.0 ml of a 0.01% (w/v) solution of HAuCl₄. All chemicals were purchased from Sigma-Aldrich. The mixture was stirred for 5 min under gentle boiling, cooled to room temperature, and stored at 4 °C. The remaining suspensions of gold nanoparticles were similarly prepared. The initial gold concentration was 52 mg/l. Size distribution of the gold nanoparticle suspensions, determined using dynamic light scattering, is given in Figure 1(IV). The average gold concentration measured by ICP analysis is 43 mg/l, which is roughly similar to the initial concentration.

b. Catalytic experiments

Typical experiments were run at room temperature for up to 24 h inside closed vessels. Each experiment was repeated at least twice, some experiments were performed in triplicates. The reactor vessel is a 150 nm stainless-steel cylinder with a lid that has a gas inlet and has a back-pressure valve (Figure S1). A 20 cm high Teflon cylinder was used inside the reactor so that the membrane was not in contact with the steel wall and the reaction was performed in metal-free environment. The 2 mm thick ceramic membrane was placed at the bottom of the cylinder. The membrane was lying on concentric rings resulting in an empty volume open to the air so the reagents passing through the membrane are flowing out. Application of 5 bars additional nitrogen pressure resulted in extraction of reaction products through the membrane. And even so, the pore sizes in the membrane are small enough to hold the gold nanoparticles inside the vessel for further use.

Between experiments, the reactor was dismantled and washed twice with deionized water (DIW) and acetone. The membrane was visually inspected and soaked in a 2 M hypochloric acid overnight. Before the experiment the reactor was assembled and washed by transmembrane flux of pure acetone for at least 30 min. The generation of equimolar amounts of hydrogen gas was quantified in a separate experiment, carried out in a glass vessel connected to an upside-down burette. The amounts of H₂ evolved were 25.0 ml (dimethylphenylsilane), 32 ml (triethylsilane), 16.5

ml (diphenylmethylsilane), 13.0 ml (triphenylsilane) and 22.0 ml (triisopropylsilane), which are in agreement with the amount of silanes converted.

Unless stated otherwise, chemicals were purchased from commercial sources (>98% pure) and used as received. The reagents were weighed on semi-analytical balance and poured into the reactor. The gold nanoparticles were held in the membrane reactor by a porous ceramic membrane placed in the bottom (SEM image in Figure S2). The reactor was closed and the reagents were mixed inside the vessel by a magnetic stirrer at 400 rpm. The reaction products were extracted by pressurizing the vessel with 5 bar additional pressure to fill the 1.5 ml sample vials. The pressure was released by opening back-pressure valve until the pressure inside the vessel returned to normal. At the end of experiment the vessel was dismantled and all parts were washed twice with deionized water and with acetone.

Example: oxidation of dimethylphenylsilane is provided as a representative example. Acetone (7.6 ml), DIW (4 ml), 0.2 g dimethylphenylsilane and 0.2 g toluene were added to the initial suspension of gold nanoparticles in a vial at room temperature. The vial was gently mixed and its content was poured into the reaction vessel. The collected samples were analyzed immediately by an Interscience GC-8000 gas chromatograph with a 100% dimethylpolysiloxane capillary column (VB-1, 30m × 0.325mm) and a flame ionization detector. GC conditions: isotherm at 80 °C (1 min); ramp at 30 °C min⁻¹ to 280 °C; isotherm at 280 °C (3 min). The product silanol was identified by injecting standard compound, GC-MS and NMR.

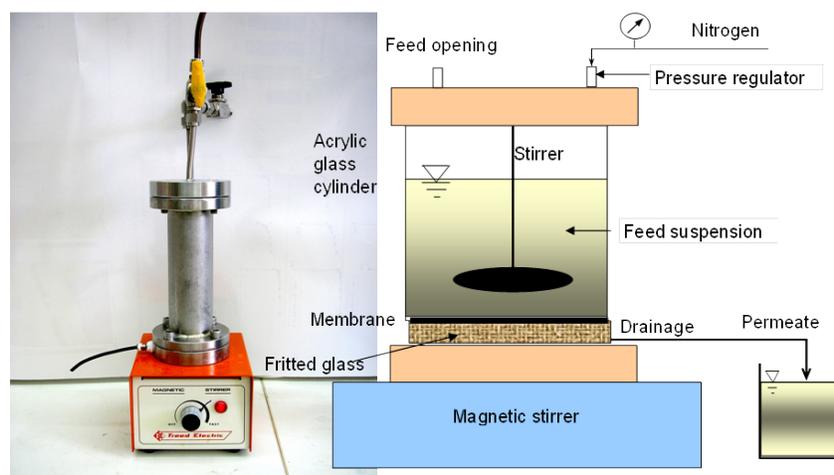


Figure S1. The membrane reactor setup for the oxidation of silane to silanol using gold nanoparticles.

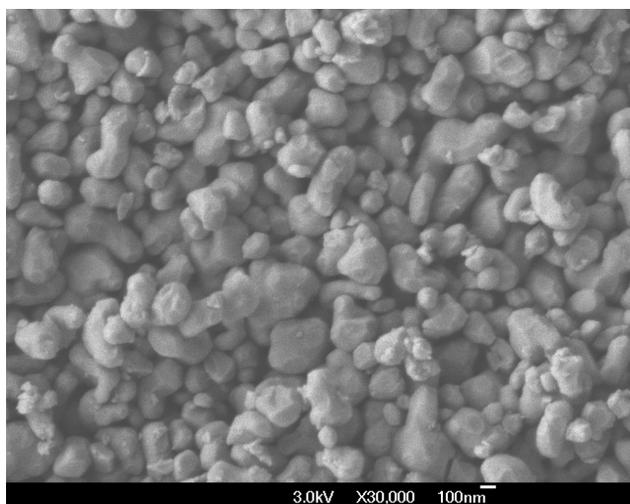


Figure S2. SEM image of the ceramic membrane used in the membrane reactor.

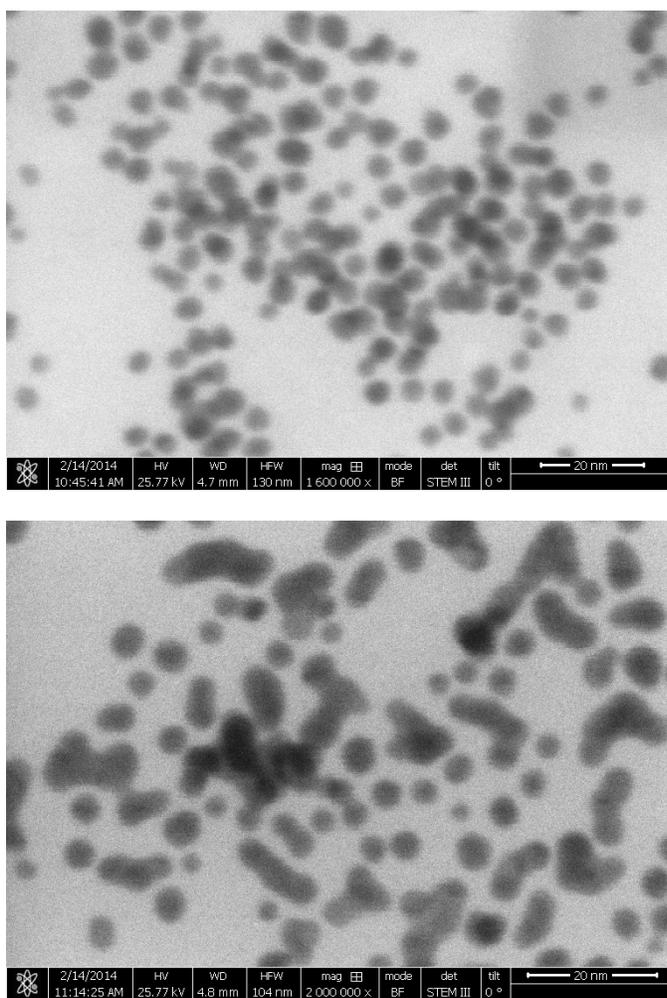


Figure S3. STEM images of gold nanoparticles before reaction (top) and after 6h reaction (bottom).

Product Characterization

GC-MS analysis was performed using a Agilent 6890, Agilent 5973 Network Mass Elective Detector system, equipped with a 30m x 0.25 mm i.d. Restex RTX® - Amine fused silica capillary column, coated with Crossbond® 5%/diphenyl 95%demethylpolysiloxane at 0.25 µm film thickness. The GC oven was programmed to start at a constant temperature of 60 °C for one minute, then to reach a temperature of 300 °C at a rate of 12 °C/min and held for three minutes. Under these conditions, the retention times were around 5.3 minutes for triisopropylsilanol (TIPS), 5.4 minutes for dimethylphenylsilanol (DMPS), 7.9 minutes for triethylsilanol (TES), 12.0 minutes for diphenylmethylsilanol (Ph₂MS) and 16.9 minutes for triphenylsilanol (Ph₃S). Products were analyzed by electron ionization (EI) mass spectroscopy (MS).

¹H NMR and ¹³C NMR spectra were recorded on a 400 MHz ¹H (100 MHz ¹³C) Bruker AV400 spectrometer in CDCl₃. Chemical shifts are reported in ppm (δ) relative to CDCl₃ (¹H: 7.26 and ¹³C: 77.36). Coupling constants, *J*, are reported in Hz. Abbreviations are used to express multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

Dimethylphenylsilanol, 2a

¹H NMR δ_H(400 MHz; CDCl₃) 7.67 – 7.34 (5 H, m, Ph), 2.21 (1 H, br s, OH), 0.41 (3 H, s, CH₃); ¹³C NMR δ_C(100 MHz; CDCl₃) 140.13, 133.33, 129.59, 128.05, 1.22; MS (EI): m/z 152 (M⁺, 9%), 137 (100), 77 (3), 75 (3), 45 (6).

Triethylsilanol, 2b

¹H NMR δ_H(400 MHz; CDCl₃) 1.25 (1 H, br s, OH), 0.92 (9 H, t, *J* 8.0, CH₃), 0.51 (6 H, q, *J* 8.0, CH₂); ¹³C NMR δ_C(100 MHz; CDCl₃) 7.17, 6.76; MS (EI): m/z 131 (M⁺-H, 75%), 117 (15), 115 (15), 103 (100), 76 (2), 45 (10).

Diphenylmethylsilanol, 2c

¹H NMR δ_H(400 MHz; CDCl₃) 7.77 – 7.32 (10 H, m, Ph), 3.45 (1 H, br s, OH), 0.71 (3 H, s, CH₃); ¹³C NMR δ_C(100 MHz; CDCl₃) 137.44, 134.29, 130.10, 128.17, 77.36, -0.96; MS (EI): m/z 214 (M⁺, 16%), 199 (100), 137 (11), 77 (7), 45 (5).

Triphenylsilanol, 2d

¹H NMR δ_H(400 MHz; CDCl₃) 7.87 – 7.12 (15 H, m, Ph), 4.75 (1 H, br s, OH); ¹³C NMR δ_C(100 MHz; CDCl₃) 135.36, 135.31, 130.42, 128.22; MS (EI): m/z 276 (M⁺, 58%), 199 (100), 122 (20), 77 (15), 45 (5).

Triisopropylsilanol, 2e

¹H NMR δ_H(400 MHz; CDCl₃) 2.64 (1 H, br s, OH), 1.44 – 1.15 (3 H, m, CH), 1.15 – 0.76 (18 H, m, CH₃); ¹³C NMR δ_C(100 MHz; CDCl₃) 17.56, 12.61; MS (EI): m/z 174 (M⁺, 5%), 131 (100), 89 (10), 45 (23), 43 (6).

References:

(1) Duek, A.; Arkhangelsky, E.; Krush, R.; Brenner, A.; Gitis, V. *Water Res.* **2012**, *46*, 2505, and references cited therein.