Supplementary Information

Highly efficient aerobic oxidation of alkenes over unsupported nanogold

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Experimental Section

Representative procedure for the preparation of Au-Si NPs

5 mL of an aqueous solution of hydrogen tetrachloroaurate (49 mg, 0.14 mmol) was mixed with 15 mL of a tetraoctylammonium bromide solution in toluene (368 mg, 0.7 mmol). The two-phase mixture was vigorously stirred until all the tetrachloroaurate was transferred into the organic phase. 10 equivalents of the stabilizing silane ligand (n-octylsilane, 20 mg, 1.4 mmol) were further added to the reaction mixture. 5 mL of an aqueous solution of 12 equiv. of sodium borohydride (64 mg, 1.7 mmol) was slowly introduced during 10 minutes under stirring. After further stirring for 3 h, the organic phase was separated and evaporated under vacuum (10^{-3} mbar). To remove the transfer agent, the excess of silane ligand and the reductant from the Au colloid, the following steps were repeated 3 times: 30 mL of ethanol were added, the colloid was precipitated at -30°C overnight and the supernatant was removed. Finally, the colloid was dried under vacuum, 5 mL of THF were further added and the colloid suspension was filtered using a micro filter (0.40μm), yielding small clean gold nanoparticles (30% yield).

Chemical analyses

Gold loadings are determined by inductively-coupled plasma optical emission spectroscopy (HORIBA Jobin Yvon Activa ICP-OES).

TEM

Transmission electron microscopy is carried out on a JEOL 2010 LaB6 microscope operating at 200 kV. Size distributions are obtained by direct observation on bright field images of carbon coated copper grids impregnated with one drop of the colloidal solution. Dispersion of gold atoms is determined from the mean particle diameter by assuming a typical cuboctahedron geometry of the gold particle. Hence dispersion is 36% for the reference catalyst, 58% for **Au-SiC$_8$** and **Au-N$^+$(C$_8$)$_4$**, and 61% for **Au-SC$_8$**.

FTIR

The **Au-SiC$_8$** colloidal solution in toluene was analyzed by Fourier-transformed infra-red spectroscopy, using a Nicolet 550-FT spectrometer. Typically, 16 scans were accumulated for each spectrum (resolution 4 cm^{-1}).

XPS

Au-SiC$_8$ particles (dried under vacuum) were analyzed by X-ray photoelectron spectroscopy is carried out on a Kratos Axis Ultra DLD spectrometer using monochromated Al Kα X-rays (1486.6 eV, 150 W) in ultra-high vacuum ($P < 10^{-9}$ mbar), a pass energy of 20 eV, analytical slot of 700 μm × 300 μm and charge compensation. The peaks (Au 4f, Si 2p, C 1s, O 1s) are referenced to the C 1s main band at 284.6 eV.

Catalytic evaluation is carried out in round-bottom flasks for 72 h in air at atmospheric pressure. Methylcyclohexane (solvent, 20 mL / 155 mmol) is added to a given amount of the colloidal solutions (Au catalyst: 2.1±0.1 µmol / 331 or 300 mg Au-SiC$_8$, 113.3 or 103.7 mg Au-SC$_8$ and 965.8 or 965 mg Au-N$^+$(C$_8$)$_4$) followed by introduction of the alkene (substrate, 1 mmol / 186 mg *trans*-stilbene 97% or 101 μL cyclohexene 99%) and TBHP (initiator, 0.05 mmol / 7 μL of a 70% TBHP solution in water from Aldrich or 9.1 μL of a 5-6 M TBHP solution in decane from Aldrich for cyclohexene oxidation) at room temperature. The resulting mixture is brought to 80°C for the oxidation of stilbene (70°C for the oxidation of cyclohexene) under stirring (900 rpm). Products are analyzed by Gas Chromatography (Shimadzu GC-2014), using an Equity TMS 30 m x 0.25 mm x 0.25 µm column programmed from 40°C to 180°C, an injector and FID detector set at 280°C and 200°C respectively, and He as carrier gas (26.6 mL min^{-1}). External calibration is carried out by injecting standard solutions of the following chemicals in acetonitrile: cyclohexene (99% Aldrich), cyclohexene oxide (98% Fluka), cyclohexen-1-ol (95% Aldrich), cyclohexen-1-one (98% Fluka), *trans*-stilbene (97% Avocado), benzil (99% Acros), deoxybenzoin (97% Alfa Aesar), benzaldehyde (98% Acros) and methylcyclohexan-1-ol (96% Aldrich). Alkene conversions and oxidation product yields are ratios of the number of mole of alkene converted and the number of mole of product formed both over the initial number of mole of alkene introduced at the beginning of the reaction. Selectivity is defined as the ratio of yield over conversion. Turnover frequencies (TOF) are defined as the number of mole of alkene converted per mole of surface gold per hour. They are calculated from the reaction rates by taking into account the gold dispersion derived from TEM analysis.

Results

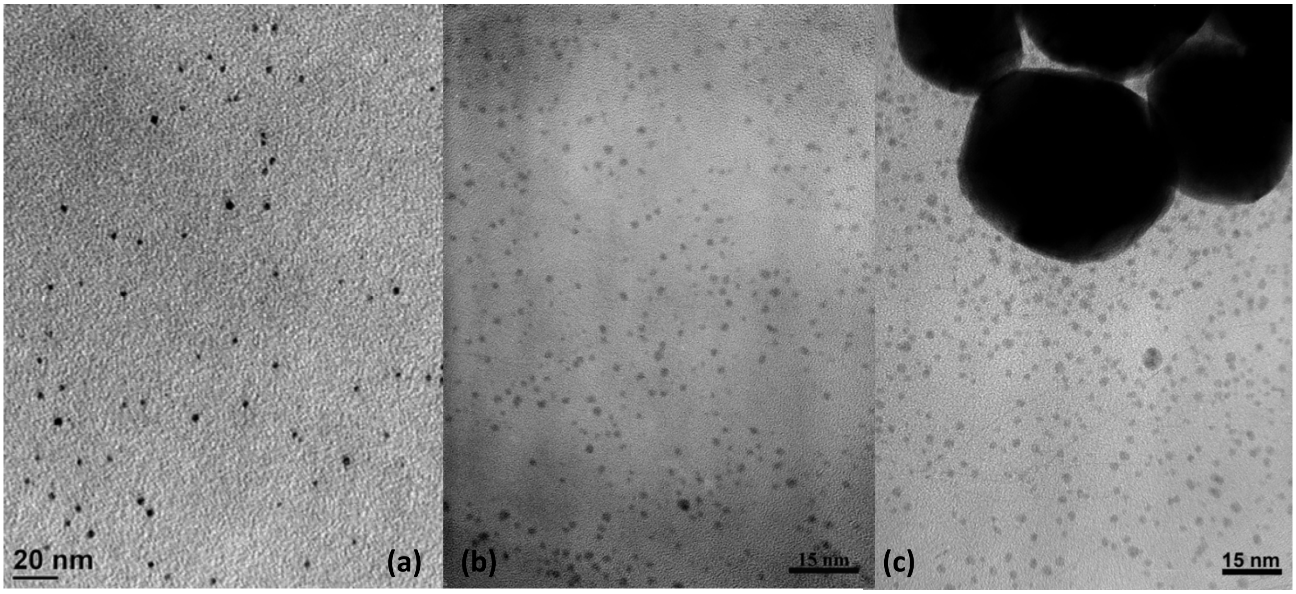


Figure S1: TEM pictures of **Au-SiC$_8$** (a), **Au-SC$_8$** (b) and **Au-N$^+$(C$_8$)$_4$** (c)

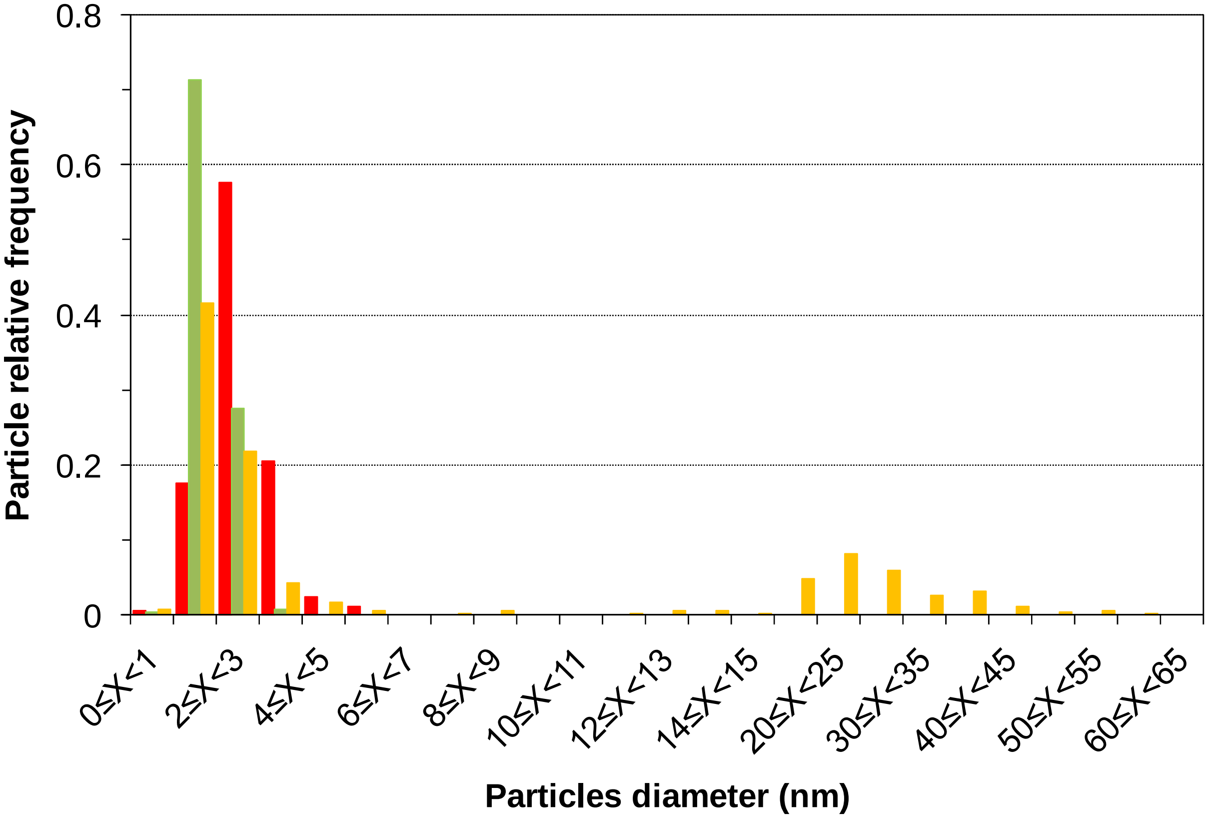


Figure S2: Gold particle size distributions as determined by TEM analysis of **Au-SiC$_8$** (red), **Au-SC$_8$** (green) and **Au-N$^+$(C$_8$)$_4$** (yellow)

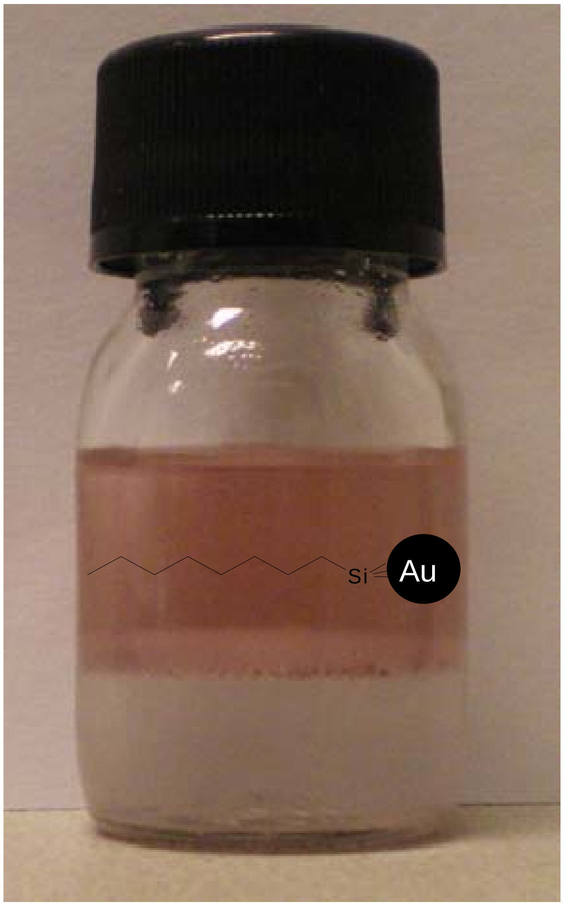


Figure S3: Picture of an aliquot of the **Au-SiC$_8$** colloidal solution in a water/heptane mixture

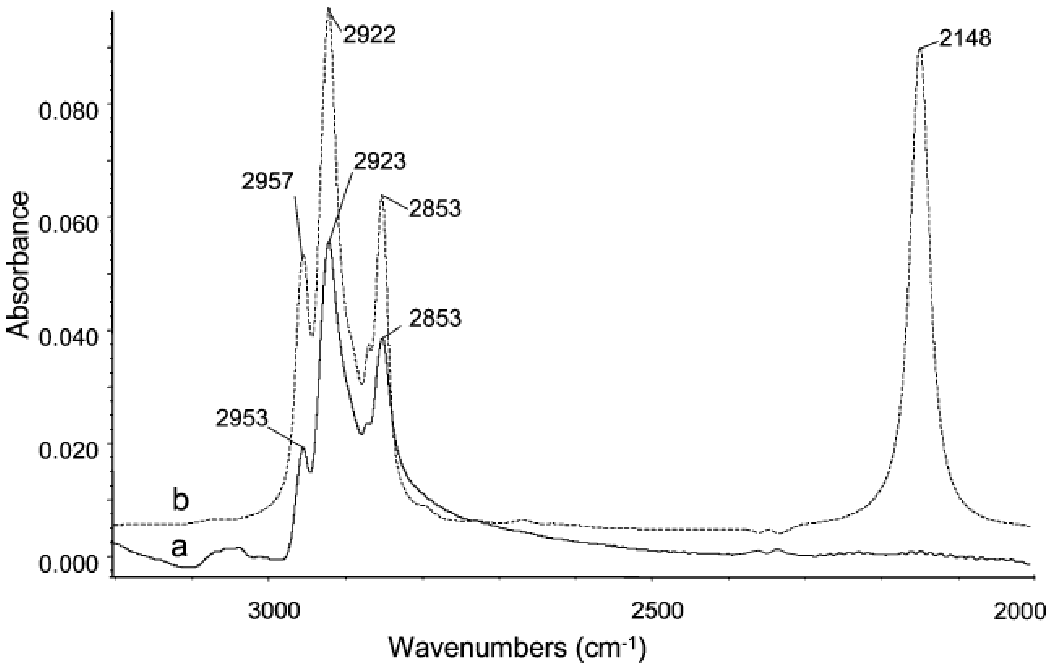
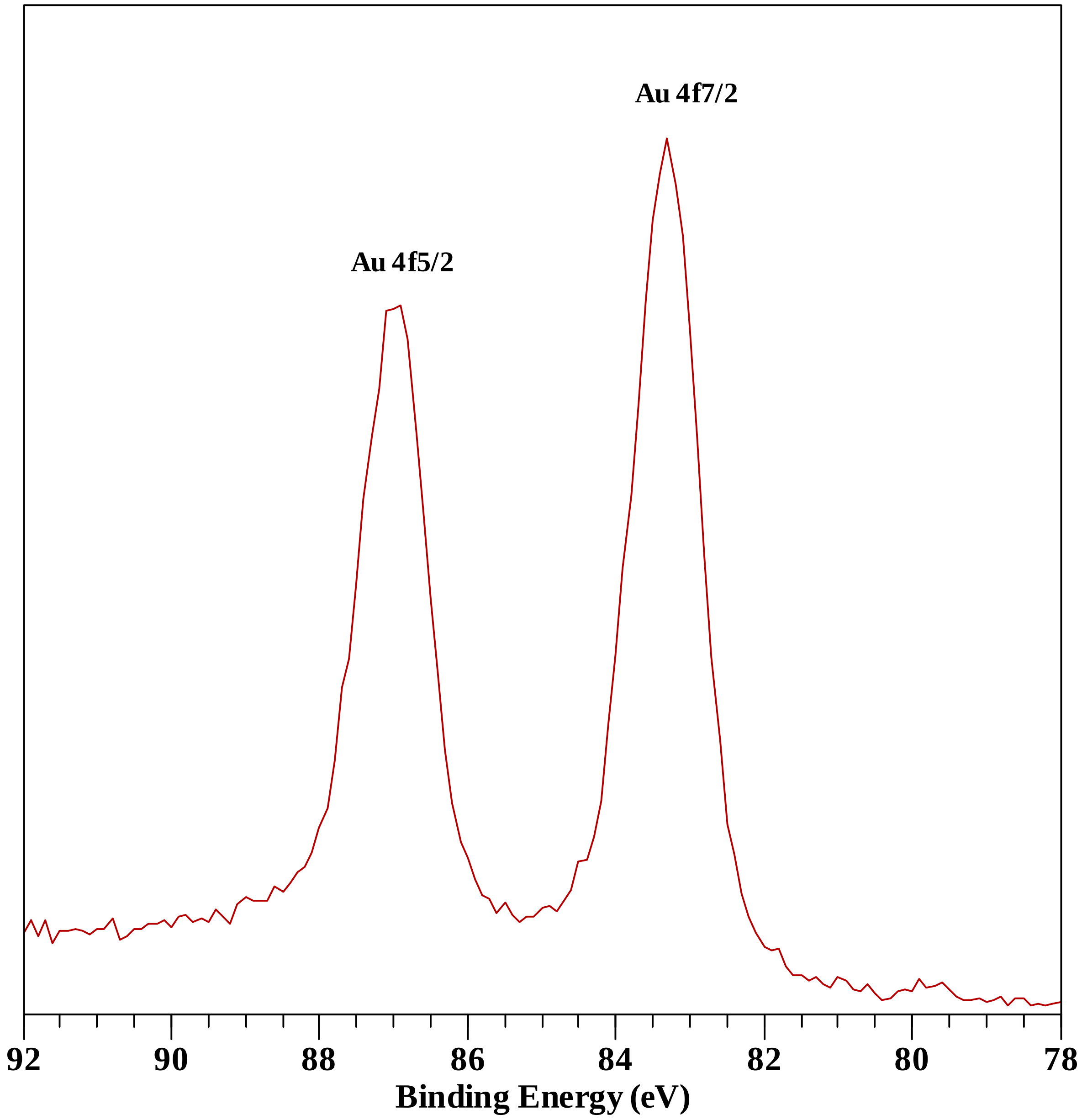


Figure S4: Infrared spectrum of (a) an aliquot of **Au-SiC$_8$** colloidal solution and (b) pure octylsilane


Au 4f7/2
Au 4f5/2
92
90
88
86
84
82
80
78
Binding Energy (eV)

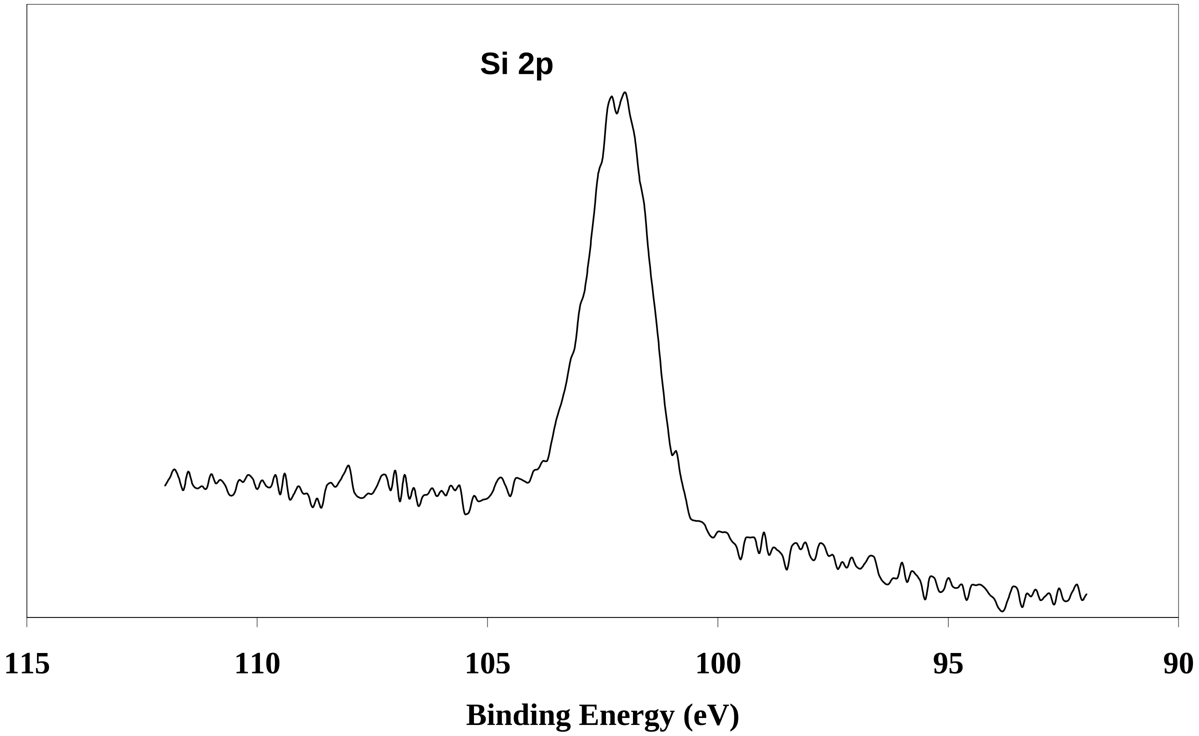


Figure S5: XPS spectra of Au 4f and Si 2p core levels in **Au-SiC$_8$**

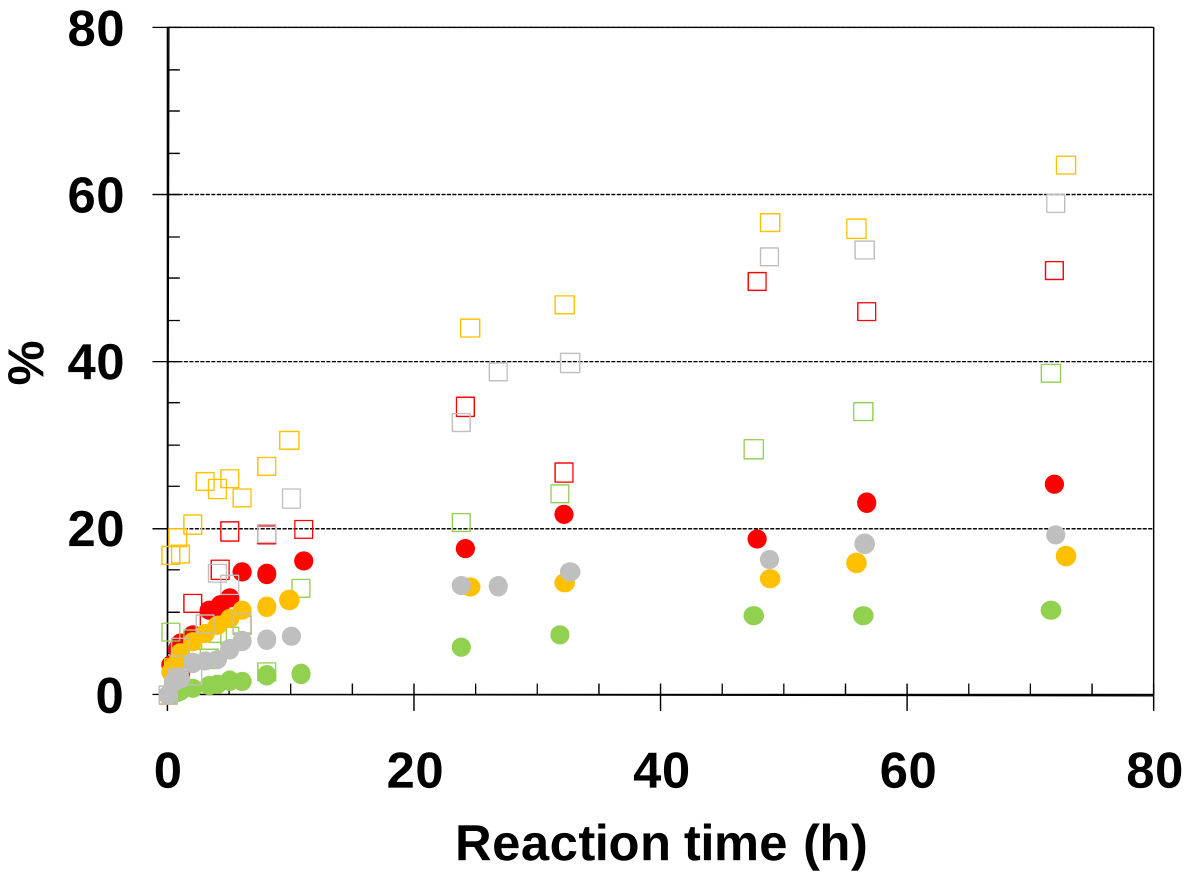


Figure S6: Cyclohexene conversion (squares) and cyclohexen-1-one yield (circles) observed over **Au-SiC$_8$** (red), **Au-SC$_8$** (green), **Au-N$^+$(C$_8$)$_4$** (yellow) and **Au/TiO$_{2\text{-WGC}}$** (grey)

Other oxidation products detected include methylcyclohexen-1-ol (in a 1 to 2 ratio as compared to cyclohexen-1-one), other minor allylic oxidation products and cyclohexene oxide (<1-2%)*, accounting for a maximum of 75% of the final cyclohexene conversion. Besides, in the absence of a gold catalyst, 20% of the cyclohexene molecule is transformed after 72 h at 70°C but no oxidation products is detected. The conversion of cyclohexene unaccounted for by GC-detected oxidation products is thus attributed to thermal degradation of the molecule, as already discussed for the oxidation of stilbene (ref 4 in the manuscript, i.e. P. Lignier, F. Morfin, S. Mangematin, L. Massin, J.-L. Rousset and V. Caps, *Chem. Commun.*, 2007, 186; P. Lignier, F. Morfin, L. Piccolo, J.-L. Rousset and V. Caps, *Catal. Today*, 2007, **122**, 284; P. Lignier, S. Mangematin, F. Morfin, J.-L. Rousset and V. Caps, *Catal. Today*, 2008, **138**, 50.).

*It is noted that, under our conditions, cyclohexene oxide yields always remain below 1-2%, unlike gold-catalyzed oxidations of cyclohexene performed under different conditions (see M. D. Hughes, Y.-J. Xu, P. Jenkins, P. McMorn, P. Landon, D.I. Enache, A.F. Carley, G.A. Attard, G.J. Hutchings, F. King, E.H. Stitt, P. Johnston, K. Griffin and C.J. Kiely, *Nature*, 2005, **437**, 1132.)