Supplementary Data for:

Propane reacts with O_2 and H_2 on gold supported TS–1 to form oxygenates with high selectivity

Juan J. Bravo-Suárez,[a] Kyoko K. Bando,[a] Tomoki Akita,[b] Tadahiro Fujitani,[a] Timothy J. Fuhrer,[c] and S. Ted Oyama*[a,c]

[a] *Research Institute for Innovation in Sustainable Chemistry, National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, 305-8569, Japan. Fax: +81 29 861 8482*

[b] *Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST), Midorigaoka 1-8-31, Ikeda 563-8577, Osaka, Japan*

[c] *Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA. Fax: +1 540 231 5022; Tel: +1 540 231 5309; E-mail: oyama@vt.edu*

Experimental section

TS–1 titanosilicates with different Ti/Si ratios (Ti/Si = 2/100, 3/100 and 10/100) were prepared by adjusting the amount of the Ti-containing reagent in a method similar to that of Uguina et al. composed of consecutive hydrolysis-condensation, gelation, wetness-impregnation, and crystallization steps.[1] The solids were separated by filtration, washed with water, vacuum-dried at 363 K for 24 h, and calcined at 773 K (2 K min^{-1}) for 5 h in air.

Gold supported catalysts were prepared by a deposition-precipitation (DP) method similar to that reported by Lu et al.[2] In a typical preparation, 150 ml of a gold solution (1 g $HAuCl_4 \cdot 4H_2O$, Wako, 99+%, in 1 L of water, 2.4 x 10^{-3} M) was heated to 343 K under vigorous stirring. The pH of the solution was adjusted to 8.8 by drop-wise addition of a 1 M Na_2CO_3 solution. After this, 1.5 g of the support was added, and the suspension was stirred for 0.25 h, followed by the addition of $Ba(NO_3)_2$ (75 mg) in water (7.5 cm^3) and stirring was continued by another 0.75 h at 343 K. Solids were filtered, washed with water (Millipore, 150 mL), dried under vacuum overnight at 298 K, and calcined under air at 673 K (~3 K min^{-1}) for 3 h. The Au/TiO_2 catalyst was prepared by a similar procedure using TiO_2 (P25) as the support, without the addition of $Ba(NO_3)_2$, and employing 0.6 L of washing water.

Catalyst powder sample was loaded in a quartz tubular microreactor of 6 mm diameter and 180 mm length using powder catalyst samples without dilution (~ 400 mg). The empty space before and after the catalyst sample was filled with glass wool to avoid gas phase reactions. Flow rates of gases were regulated by mass flow meters. The reactor was equipped with an axial quartz thermocouple well (2 mm outer diameter) which allowed monitoring of the catalyst bed temperature. Reactor temperature was maintained by an electronic controller. The catalyst was pretreated in Ar at 443 K for 0.5 h, after which C_3H_8, H_2, and O_2 in Ar were introduced. Reaction products were analyzed online using two chromatographs after 0.5 h. A detailed description of the analytical system can be found elsewhere.[2]

Transmission electron microscopy images of the samples were obtained in a microscope (Hitachi H-9000) operated at 300 kV. Ex situ Au L_3-edge X-ray adsorption fine structure measurements were carried out at beamlines BL-9A (transmission mode) and AR-NW10A (fluorescence mode) of the Photon Factory in the Institute of Materials Structure Science, High Energy Accelerator Research Organization (PF-IMSS-KEK) in Japan. In situ UV-vis spectra were collected under reaction conditions using a large compartment spectrometer (Varian Cary 5000) equipped with a Harrick Scientific reaction chamber (Model HVC-DRP) and a praying mantis diffuse reflectance attachment (DRP-XXX). Ammonia and CO_2 temperature-programmed desorption measurements were carried out at 373 K in a chemical adsorption flow unit (BEL-CAT). Adsorbed amounts were calculated by comparing desorption peak areas with calibration values from pulses of a known volume of the studied gas.

Density functional theory (DFT) calculations were conducted using the Gaussian 98 [1] or Gaussian 03 [2] suite of programs. We used electronic DFT with Becke’s three-parameter formulation with Lee, Yang and Parr’s gradient-corrected functional (B3LYP) [3-4] with the 6-311G(2d,p) basis set.

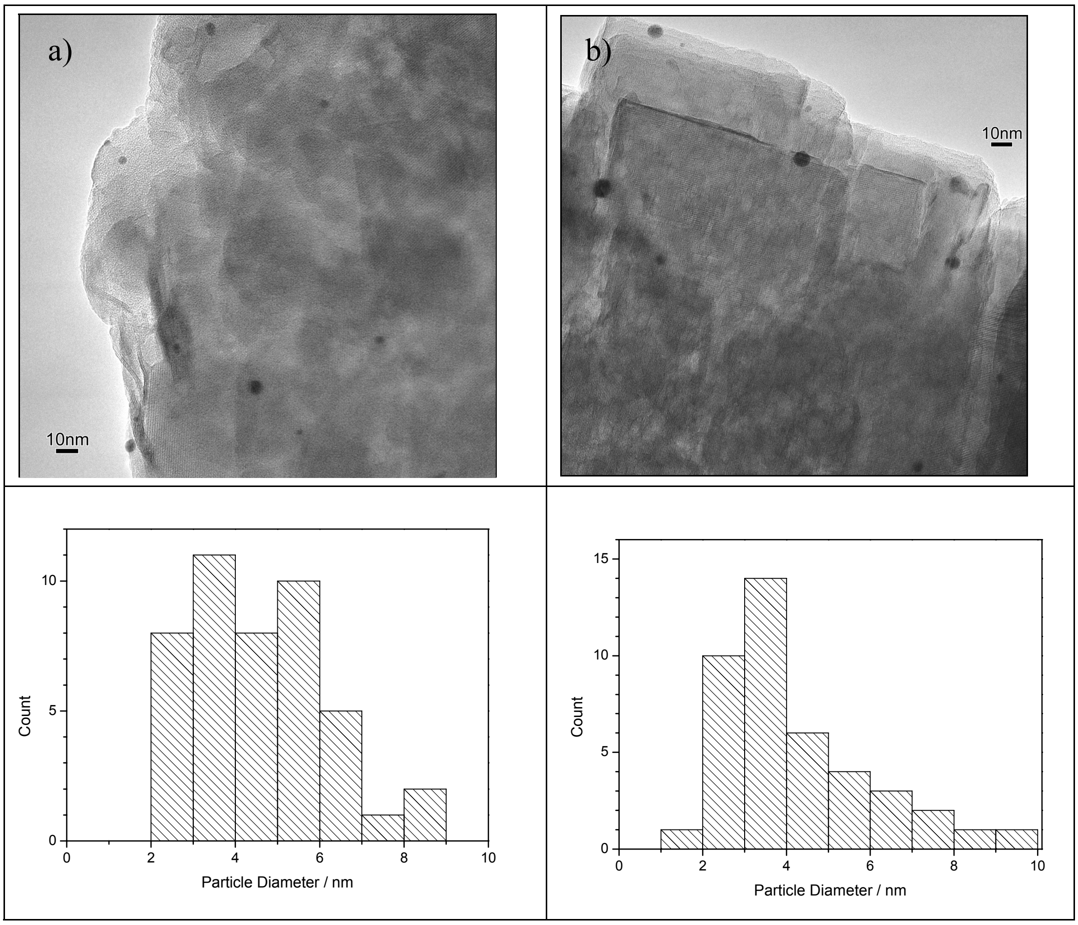

Fig. S1. TEM micrographs and particle size distributions for Au–Ba/TS–1 catalysts: a) Ti/Si = 2/100, and b) Ti/Si = 3/100.

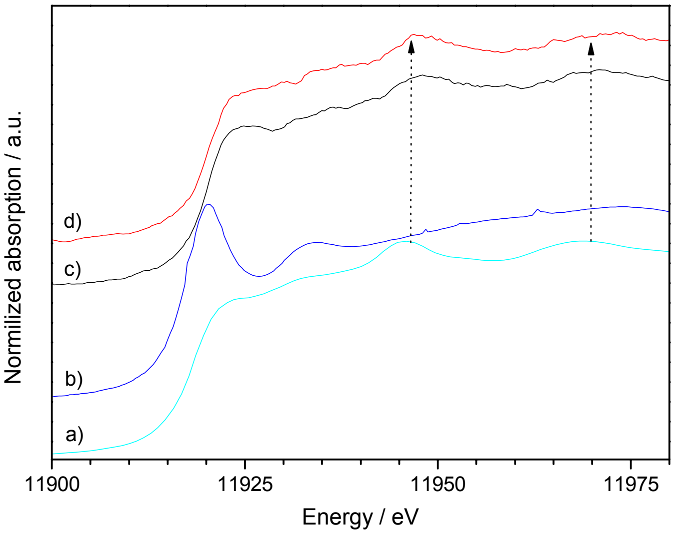

Fig. S2. Ex situ Au L$_3$-edge XANES for a) Au foil, b) HAuCl$_4$, c) Au–Ba/TS–1 (Ti/Si=3/100), d) Au–Ba/TS–1 (Ti/Si=10/100).

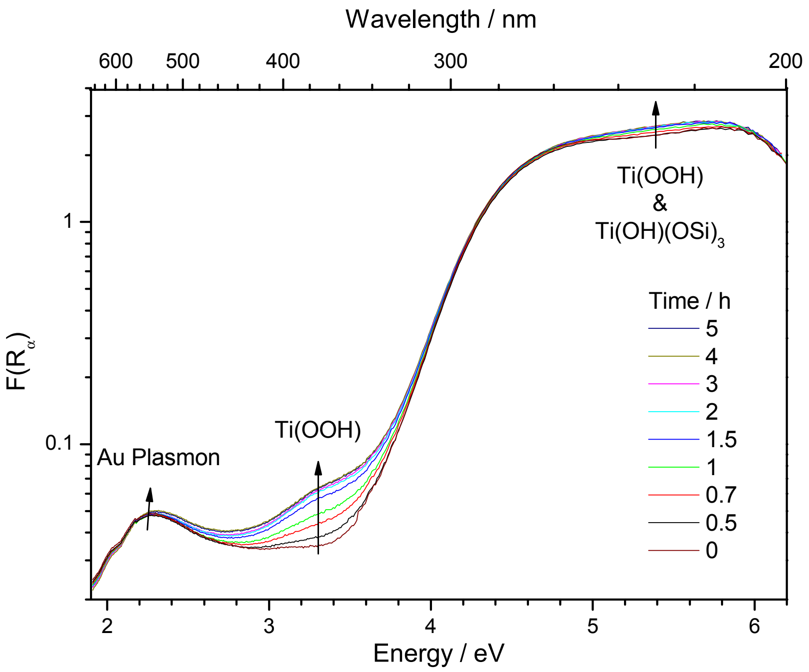

Fig. S3. In situ UV-vis spectra for Au–Ba/TS–1 (Ti/Si = 3/100) under $C_3H_8/H_2/O_2/Ar$ at 443 K and 0.3 MPa. Spectra at time 0 h is for the catalyst under Ar just before reaction. Referenced to $BaSO_4$.

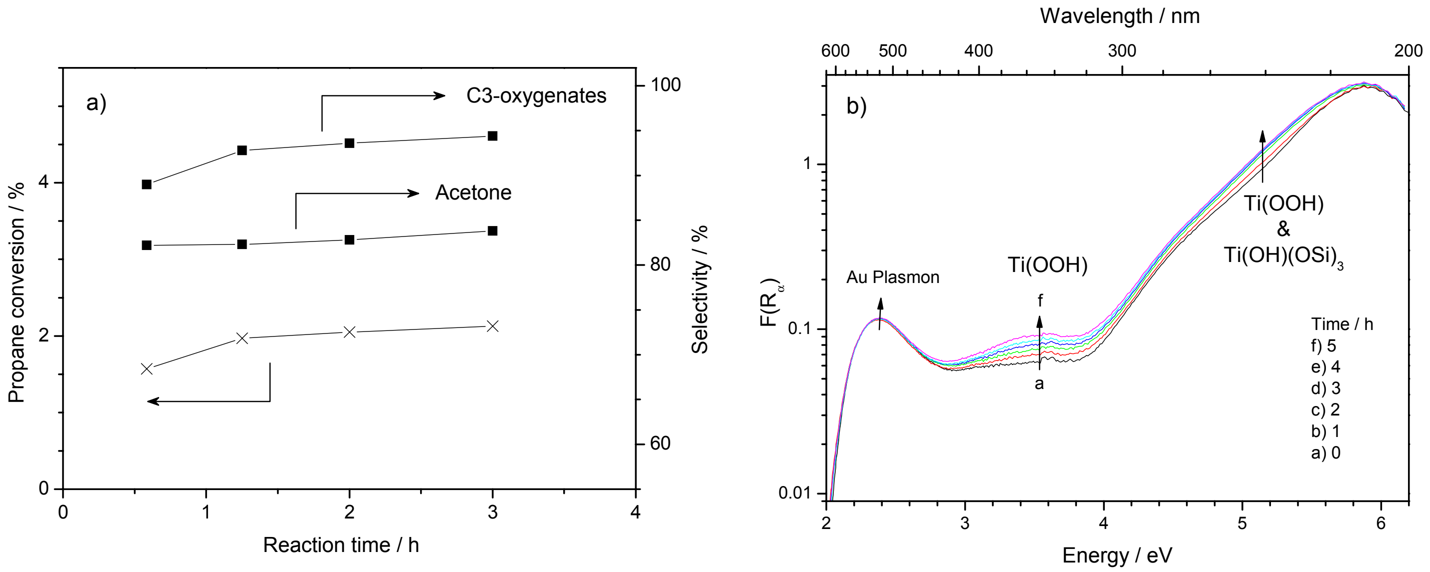

Fig. S4. a) Propane conversion and C3-oxygenates (acetone and isopropanol) selectivity over a 0.52 wt% Au/TS–1 (Ti/Si = 3/100) catalyst with reaction time on stream. b) In situ UV–vis spectra under propane oxidation conditions as a function of time. Spectra at time 0 h is for the catalyst under Ar just before reaction. Reaction conditions: $C_3H_8/H_2/O_2/Ar$ = 1/1/1/7, 443 K, 0.1 MPa, reactor SV = 12000 cm^3 h^{-1} g$_{cat}^{-1}$. Spectra were referenced to $BaSO_4$.

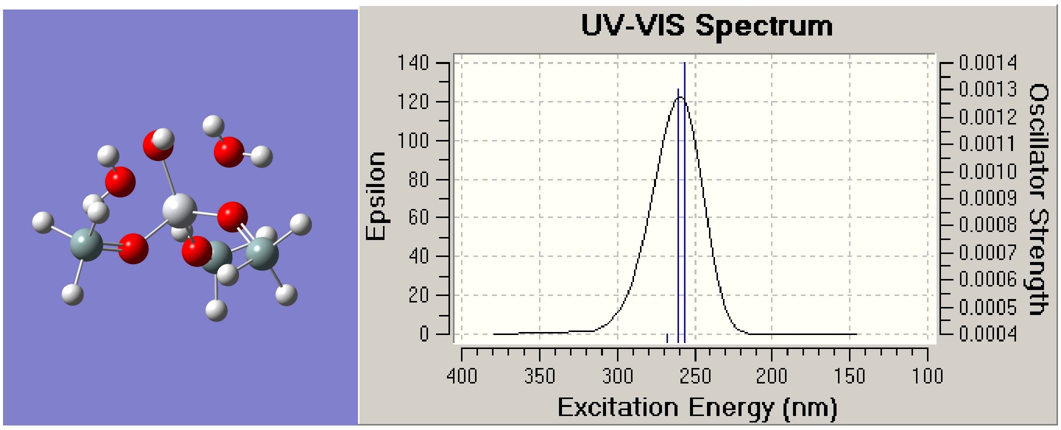

Fig. S5. DFT Calculations on $Ti(OH)(H_2O)(OSi)_3$ showing UV band at 260 nm.

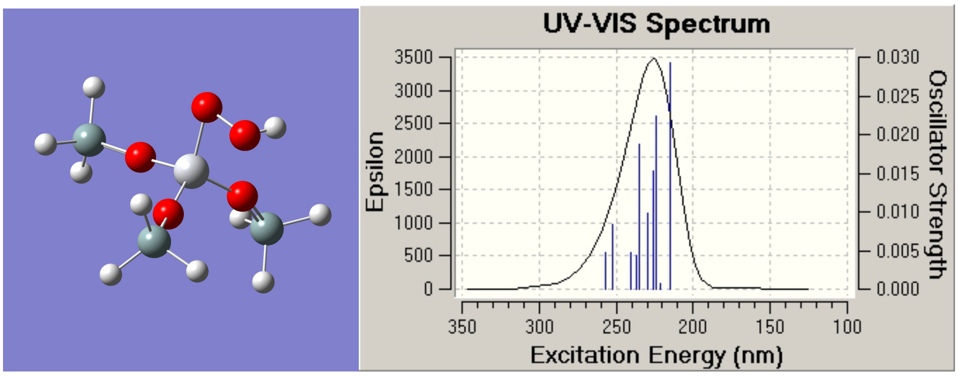

Fig. S6. DFT Calculations of $Ti(OOH)(OSi)_3$ showing UV band at 225 nm.

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[1] M. A. Uguina, D. P. Serrano, G. Ovejero, R. Van Grieken, M. Camacho, *Appl. Catal., A* 1995, **124**, 391.

[2] J. Q. Lu, X. Zhang, J. J. Bravo-Suárez, K. K. Bando, T. Fujitani, S. T. Oyama, *J. Catal.* 2007, **250**, 350.