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

J. J. Bravo-Suárez,[a] K. K. Bando,[a] T. Akita,[b] T. Fujitani,[a] T. J. Fuhrer[c] and S. T. Oyama*[ad]

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Gold nanoparticles supported on a microporous titanosilicate (TS-1) were found to be highly selective (95%) towards the formation of acetone and isopropanol from propane, O_2, and H_2 at moderate temperatures (443 K).

Propane partial oxidation to high value products has been a long sought goal. Examples of such products include acrylic acid and acrylonitrile,[1] as well as acetone and isopropanol. Acetone, for example, is mainly produced as a co-product in the synthesis of phenol by the cumene process, with a world production of 5.2 million metric tons in 2004.[2] Future planned processes for directly obtaining phenol from benzene will necessitate alternative routes for acetone.[3] Isopropanol is produced by hydration of propylene using acid catalysts, with a total world capacity of 1.9 million metric tons in 1996.[4] This process requires high pressures and suffers from corrosion problems. Alternative acetone and isopropanol production methods from propane have been studied. In these methods, propane reacts with O_2 or hydroperoxides at mild temperatures and high pressures using biomimetic complexes (*e.g.*, Fe, Co, or Cu porphyrins, phthallocyanines, and oxometallates)[5–9] or Ti, V, or Fe containing catalysts.[6–9] An ideal process from low-cost abundant propane should be continuous, produce oxygenates with high selectivity, use O_2 as the oxidant at moderate conditions, and use a recyclable catalyst. None of the above methods fulfils all these requirements.

Here it is shown that propane can be converted continuously to acetone and, in lesser amounts, isopropanol with high selectivity (95%) under mild conditions (443 K and 0.3 MPa) using a mixture of O_2 and H_2 as the oxidizing agent and Au–Ba/TS-1 as the catalyst. Evidence is presented for the presence of intermediates during the reaction, including adsorbed oxygen on Au and hydroperoxide species on Ti.

The Au–Ba/TS-1 catalysts were prepared by the deposition–precipitation (DP) method[10] using Na_2CO_3 as the neutralizing agent, a pH of 9, and TS-1 as the support (see ESI for details†). Ba was added to improve the Au capture by the support.[10] The Au loadings were about 0.1 wt% and Au particle sizes about 4.0 nm (see ESI†). Propane oxidation was carried out at 443 K and 0.3 MPa, with O_2 and H_2. The catalysts (Ti : Si = 2 : 100, 3 : 100, and 10 : 100) formed mostly acetone with some isopropanol in combined selectivities of over 85% and propane conversions of 2.1–6.5% (Table 1). In particular, the Au–Ba/TS-1 catalyst with an intermediate Ti : Si = 3 : 100 ratio presented the most remarkable catalytic results with an oxygenate selectivity of 95% at a propane conversion 6.5%, which corresponded to acetone and isopropanol space-time yields (STY) of 33 and 2 g kg_{cat}^{-1} h^{-1}, respectively. The resulting acetone TOF was 0.079 s^{-1} based on exposed Au. The Au loadings in the samples were similar, with a slightly higher value for the catalyst with Ti : Si = 3 : 100. The difference in reactivities is likely due to an optimum Ti : Si ratio that allows the formation of a maximum number of effective Ti sites in the zeolite framework.[11] Here, the best Ti : Si ratio of 3 : 100 corresponds well with previously reported maximum contents of Ti in TS-1 zeolite framework positions.[12]

Catalytic oxidation with O_2 and H_2 on Au/TiO_2–SiO_2 likely occurs by *in situ* formation of H_2O_2 on Au. The H_2O_2 then transfers to Ti tetrahedral sites to form Ti–OOH species active for selective oxidations, such as propylene epoxidation.[13,14] In the case of propane, a similar mechanism may take place, and the involvement of isopropoxy intermediate species could explain the formation of acetone and isopropanol.

In situ UV-Vis spectra of Au–Ba/TS-1 (Ti : Si = 3 : 100) under propane oxidation conditions show evidence for the formation of the Ti–OOH species. Changes occur in several regions (Fig. 1 and ESI†): (1) a band at about 540 nm due to a plasmon resonance (PR) of Au nanoparticles[15] (Au is mostly metallic as evidenced by the absence in the Au L_3-edge XANES of a near-edge resonance around 11 920 eV due to oxidized Au, see ESI†); (2) band growth at 320–410 nm and 210–240 nm due to Ti–hydroperoxo species;[12,16] and (3) a band decrease at 250–300 nm due to tripodal Ti sites, $Ti(OSi)_3$–$OH{\cdot}(H_2O)_2$.[12] These assignments are supported by density functional theory (DFT) calculations (see ESI†). The Au PR position as a function of reaction time (Fig. 1a) shows an initial increase (red shift) during the first 0.1 h, followed by a decrease (blue shift), reaching a constant value (539.4 nm) after 3 h. The initial red shift is related to O_2 adsorption on Au,[17] while the subsequent blue shift is explained by reaction of O_2, most likely with H_2 to form H_2O_2. The steady-state Au PR position (539.4 nm) was higher than that observed under H_2 flow (534.1 nm), confirming the presence of adsorbed O_2 on Au during reaction. Although an adsorbed superoxide O_2^- species has been observed by electron paramagnetic resonance spectroscopy,[16] to the best of our knowledge, this is the first *in situ* experimental evidence of adsorbed oxygen on Au

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[a] *National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, 305-8569, Japan*
[b] *AIST, Midorigaoka 1-8-31, Ikeda 563-8577 Osaka, Japan*
[c] *Chemistry and Physics, Radford University, Radford, VA 24142, USA*
[d] *Chemical Engineering, Virginia Tech, Blacksburg, VA 24061, USA. E-mail: oyama@vt.edu; Fax: +1 540 231 5022; Tel: +1 540 231 5309*

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Table 1 Catalytic reactivity of Au–Ba/TS-1 catalysts for propane partial oxidation

Nominal Ti : Si ratio	[Au] (wt%)[a]	D_p/nm[b]	Conversion (%)		Selectivity (%)				H_2 efficiency (%)[c]	Main product[d]	
			C_3H_8	H_2	Acetone	2-Propanol	C_3H_6	CO_2		STY/g kg_{cat}^{-1} h^{-1}	TOF/s^{-1}
2 : 100	0.09	4.4	2.1	7	92	2	0	6	10	10	0.032
3 : 100	0.11	4.0	6.5	10	90	5	0	5	17	33	0.079
10 : 100	0.07[e]	4.2	2.5	5	83	2	0	15	42	12	0.047
10 : 100[f]	0.02	—	0.4	5	89	0	0	11	16	2	0.031
∞[g]	1.2	2.7	1.4	15	4	0	69	27	16	120	0.029

[a] Au content by ICP-AES. [b] Au average size by TEM. [c] H_2 selectivity to C_3-products. [d] (STY: space-time yield; TOF: turnover frequency) TOF based on exposed Au. Au dispersion is calculated from particle size, assuming Au fcc packing and spherical particles. [e] Estimated from Au L_3-XAFS edge-jump intensity. [f] Without Ba. [g] Au/TiO_2 (P25) with $C_3H_8 : H_2 : O_2 : Ar = 2 : 1 : 1 : 6$, 443 K, 0.1 MPa, SV (space velocity) = 36 000 $cm^3\ h^{-1}\ g_{cat}^{-1}$. Reaction conditions: $C_3H_8 : H_2 : O_2 : Ar = 0.5 : 3 : 1 : 5.5$, 443 K, 0.3 MPa, SV ~ 4500 $cm^3\ h^{-1}\ g_{cat}^{-1}$. Reactivity after 0.5 h.

supported on a titanosilicate. Propane conversion and selectivities on Au/TS-1 appeared to track with spectroscopic changes (see ESI†); however, to prove that the observed species are true intermediates would require the use of transient spectroscopic techniques.[14,18]

In situ UV-Vis spectra (Fig. 1b) initially show hydrated hydroxyl species $Ti(OSi)_3$–$OH{\cdot}(H_2O)_2$ that react (decrease in 270 nm band) with H_2O_2 to form hydroperoxide species. The latter are dehydrated Ti(OOH) (225 nm band) and hydrated Ti–OOH (360 nm band) species. DFT calculations provide the assignments (see ESI†). Overall, the *in situ* PR and UV-Vis spectroscopy results are consistent with the adsorption of oxygen on the gold nanoparticles followed by activation with H_2 to produce H_2O_2, which transfers to a Ti center to form hydroperoxide species (Scheme 1). In the scheme Au represents a gold cluster, not an isolated gold atom.

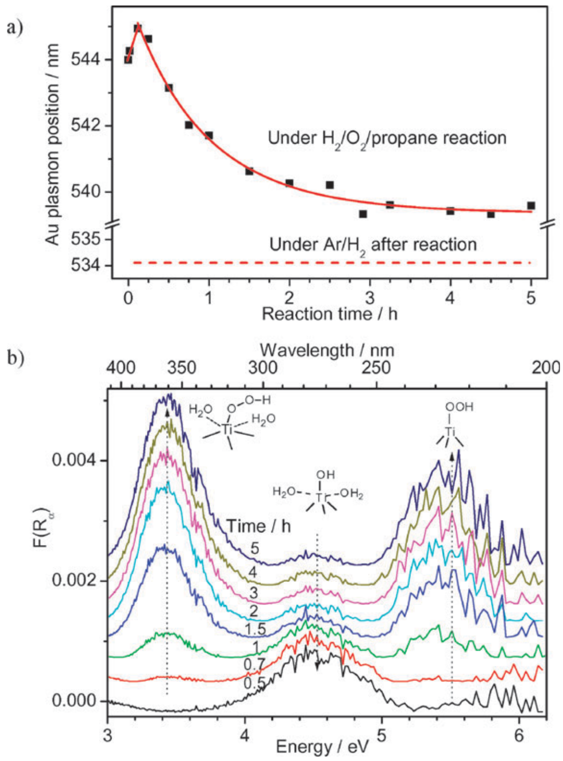
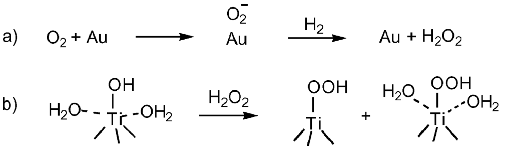


Fig. 1 *In situ* UV-Vis spectra for Au–Ba/TS-1 (Ti : Si = 3 : 100) under reaction conditions: (a) Au plasmon resonance position, and (b) difference spectra with catalyst before reaction under Ar.

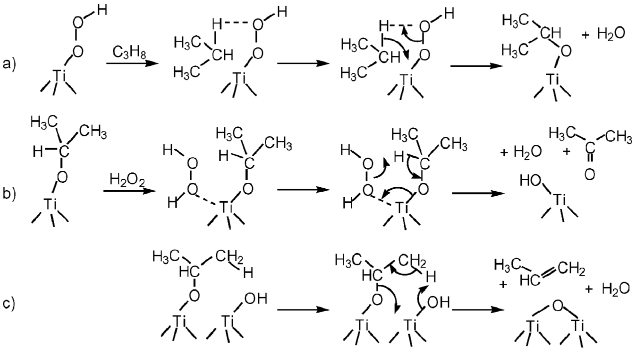


Scheme 1 Sequence of steps in oxygen activation: (a) H_2O_2 formation on gold; (b) hydroperoxide formation on Ti centers.

The main products of reaction on the gold catalysts were acetone (TS-1 support) and propylene (TiO_2 support). It has been proposed that propane activation on TS-1 yields an isopropoxy intermediate,[19] and this is likely the case for these catalysts (Scheme 2a). A 2° proton on propane (most acidic) undergoes attack by the terminal OH on the hydroperoxide, and the electrons from the C–H bond transfer to the proximal peroxide oxygen (most electropositive). The propoxy species could produce acetone (Scheme 2b) or propylene (Scheme 2c), as is observed for isopropanol on basic oxides.

The different selectivities of the TS-1 and TiO_2 supports could arise from differences in their acid–base properties.[20] Temperature-programmed desorption (TPD) traces of CO_2 and NH_3 from Au–Ba/TS-1 (Ti : Si = 3 : 100) and Au/TiO_2 catalysts, and their corresponding supports clearly show marked differences (Fig. 2). The Au–Ba/TS-1 sample mainly has small amounts of weak acid and base sites, while the Au/TiO_2 catalyst also has stronger basic and acidic sites and in larger concentrations.

Under the oxidizing conditions of the present study acetone formation is expected to proceed by reaction of the



Scheme 2 Possible sequence of steps during propane selective oxidation on gold supported Ti-containing catalysts: (a) formation of the isopropoxide intermediate; (b) oxidation of the isopropoxide species to acetone; (c) dehydration of the isopropoxide species to propylene.

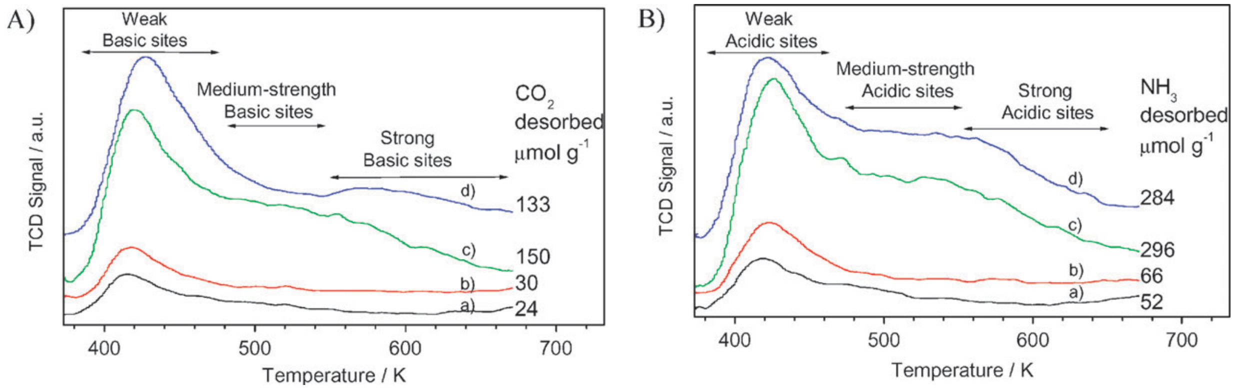


Fig. 2 (A) CO_2 and (B) NH_3 temperature-programmed desorption traces for different gold supported catalysts and supports. (a) TS-1 (Ti : Si = 3 : 100); (b) Au–Ba/TS-1 (Ti : Si = 3 : 100); (c) TiO_2 (P25); and (d) Au/TiO_2.

isopropoxide intermediate with H_2O_2 (Scheme 2b). On the other hand, propylene formation likely occurs by dehydration of isopropoxy species. In analogy with isopropanol reactions on metal oxides, this would be expected to occur on strong–weak or weak–strong acid–base pair sites present on the TiO_2 support, possibly *via* concerted E_2 or E_{1cB} mechanisms, respectively.[21] The E_2 dinuclear elimination mechanism involves transfer of a proton on the adsorbed propoxy species to a surface OH group, with simultaneous loss of the surface oxygen link (Scheme 2c).[22,23] The E_{1cB} mononuclear elimination mechanism is similar, but occurs in two steps, with the proton abstracted first.[22,23] This is unlikely in the present case because the Ti group is not a sufficiently strong base. The Ba component is probably not involved in the reaction, as unpromoted Au/TS-1 catalysts show similar conversion and selectivity. As mentioned earlier, its main role is to increase the Au loading (Table 1).[10]

Propane oxidation has been previously reported in a H_2–O_2 cell system at 298 K. Acetone (39%) and acetaldehyde (13%) were produced at a STY of only 6 g $kg_{cathode}^{-1}$ h^{-1}.[24] More recently, propane oxidation mediated by a Fe^{2+}–H_2O_2 Fenton system was carried out in a three-phase catalytic hollow fiber membrane reactor. Total oxygenate selectivity (acetone, isopropanol, *n*-propanol, and propanal) was 96%, but the STY reached only 5 g $kg_{membrane}^{-1}$ h^{-1}.[8] In the present study propane is oxidized with O_2 and H_2 to acetone and isopropanol with a high selectivity of 95% and a STY of 35 g kg_{cat}^{-1} h^{-1}, which is much higher than previously reported yields and is similar to that obtained in a batch system using costly H_2O_2 and TS-1 with a selectivity to oxygenates (acetone and isopropanol) close to 100% and a STY of 79 g kg_{cat}^{-1} h^{-1}.[9]

In conclusion, it has been demonstrated that Au supported on TS-1 are active catalysts for propane oxidation with O_2 and H_2, and highly selective towards the formation of acetone and isopropanol, with space-time yields (STY) comparable to those obtained with liquid H_2O_2 in a batch reactor.[9] These results are encouraging as further improvements in the catalytic and reactor system will likely yield much higher STYs. *In situ* spectroscopic data and catalyst characterization reveal the presence of possible reaction intermediates (O_2 adsorbed on metallic Au, Ti–OOH, and isopropoxy species) and contribute to a better understanding of gas-phase catalyzed oxidations on gold supported catalysts.

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