Isotope Labeling Study of CO Oxidation-Assisted Epoxidation of Propene. Implication on Oxygen Activation on Au Catalysts.

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Supplementary Information.

Methods

Materials:

Au/TiO_2 catalysts were supplied by the World Gold Council. Two different batches labeled Au-TiO_2-02-4 and Au-TiO_2-O2-9 were used. The Au loadings were 1.51 and 1.49 wt. % and the average Au diameters were 3.8 ± 1.5nm and 3.6 ± 1.32 nm, respectively. There was no discernible difference in the catalytic performances of the two catalysts. TS-1 was synthesized using the method of Thangaraj et al.[1] The incorporation of Ti into the silicalite framework was verified using diffuse reflectance UV visible spectroscopy (Perkin Elmer LAMBDA 1050). The Ti content was 1.0 wt. %, as determined by ICP. The silicalite sample was synthesized using the same procedure as for TS-1, except that no TiBuOH was added.

1. Thangaraj, A., Kumar, R., Mirajkar, S. P., and Ratnasamy, P., *Journal of Catalysis* **130** (1), 1 (1991).

Catalytic test

The epoxidation reaction was carried out in a Lab-Crest pressure glass reactor which was filled with 50 mL of solvent. The solvent used was either ion-exchanged distilled water or anhydrous CH_3OH, or their mixture. In some experiments, anhydrous ethanol or acetonitile was used instead of methanol. The feed gas, at a flow rate of 40 mL min^{-1}, was adjusted to the desired composition using mass flow controllers, and flowed into the liquid through a 5 μm stainless steel porous frit. The pressure in the vessel was maintained at 480 kPa with a back pressure regulator. The temperature of the liquid in the reactor was maintained at 40°C with the help of an external water bath. Before the experiment began, the catalyst mixture (typically 0.1g Au/TiO_2 and 0.15 g TS-1) was placed in a small polyethylene cup held with a small, Teflon-covered magnet above the liquid. The feed composition was adjusted, the CO oxidation activity of the catalyst was tested, and the system was allowed to reach a steady state. Then, the catalyst cup was guided by the magnet into the liquid and the liquid was stirred to commence the experiment. The exit gas was sampled regularly with a gas chromatograph. At the conclusion of the experiment, the liquid was analyzed by gas chromatography and product identity and isotope distributions were determined GC-MS (Fig. S2 – S4). The peroxide contents were determined by titration with cerium sulfate using a ferroin indicator.

Analysis of TS-1:

About 0.039 g of the TS-1 was dissolved completely in 2 mL distilled deionized (DDI) water and 3 mL 48% HF. The resulting solution was further diluted with 45 mL water, which was then analyzed using ICP-AES.

Product Analysis:

The gas phase products were analyzed by on-line gas chromatography (Agilent 6890 GC) using two columns: a carbosphere packed column with a TCD detector for analysis of CO, O_2 and CO_2, and a Econo-cap EC-Wax capillary column with a FID detector for organics. The liquid product was also analyzed by the same capillary column by injecting a small sample of the liquid with a syringe. All liquid products were separated from the solid catalysts by filtration through a 0.2 μm PVDF membrane (Pall) first before analysis. The isotope distributions were determined using a GC-MS (Agilent 6890 GC with 5973 MSD) with the FID and MSD sharing a capillary column via a splitter.

H_2O_2 and/or alkylhydroperoxide was titrated as follows. A ferroin indicator solution was prepared by dissolving 0.123 g iron(II) sulfate heptahydrate ($FeSO_4 \bullet 7H_2O$) into 15 mL DDI water, then adding 0.259 g 1,10-phenanthroline. The titration solution was prepared by dissolving 0.114 g cerium(IV) sulfate ($Ce(SO_4)_2$) into dilute sulfuric acid (1/19 v/v). Into a conical flask, 5 mL sample and 10 mL diluted sulfuric acid (1/19 v/v) were added. Two drops of ferroin indicator were added to the above solution, turning it red. The titration solution, 0.6875 mM $Ce(SO_4)_2$, was then added until a color change to pale blue was observed.

Reactor System:

The reactor was a Lab-Crest pressure glass reactor (Cole-Parmer) into which a stream of premixed gas flowed and dispersed with a 5 μm stainless steel porous frit (Scientific Instrument Services) (Fig. S1). The pressure in the reactor was maintained with a back pressure regulator (Mighty Mite). A polyethylene cup, with a metal wire wrapped around it, was used to hold the catalyst above the liquid with a magnet outside the reactor. When the external magnet was removed, the catalyst would drop into the liquid and disperse. The gas composition was adjusted using mass flow controllers (Brooks). The temperature of the reactor was maintained by placing it in a water bath.

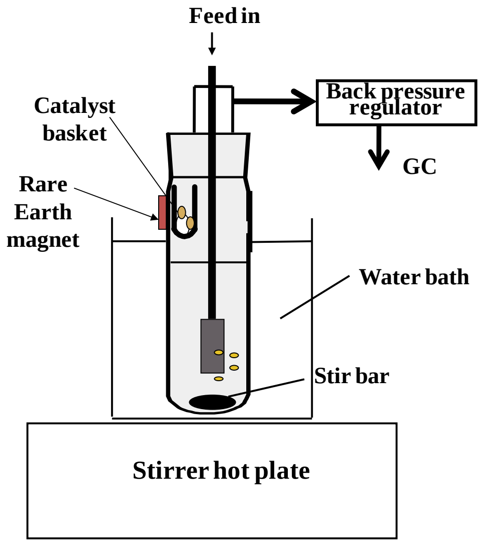

Figure S1. The reactor system.

Table S1. Summary results for liquid phase CO oxidation-assisted epoxidation of propene.

Exp.[a]	Reaction conditions		Rxn time, min.	Reaction rate,[b] μmol/min			Quantity, x10^{-5} moles[c]				PO/CO[d]
	MeOH:H_2O	CO, O_2, propene[e]		CO	O_2	Propene	Total PO, ±1	Other products[f]	Propene cons. ±2	–OOH[g] ±0.2	
1	0:50	2.5,1.25,1.6	292	2.5	1.6	0.83	2.7	14.6	24	0.34	0.04
2	40:10	2.5,1.25,1.6	232	11	5.8	0.88	21	trace	22	0.72	0.08
3		2.5,1.25,3.3	221	9.3	5.5	0.97	28	trace	22	nd	0.14
4		1.25,1.25,1.6	234	5.6	3.0	0.58	12	trace	12	nd	0.1
5	47.5:2.5	2.5,1.25,1.6	251	4.0	2.5	0.81	23	trace	20	0.37	0.22
6		2.5,1.25,3.3	235	5.5	3.6	1.1	27	trace	>26	nd	0.21
7	50:0	2.5,1.25,1.6	>100	0	0	0	0	0	0	nd	--
8 (EtOH)	47.5[h]:2.5	2.5,1.25,1.6	240	1.8	1.1	.08	1.5	trace	2	nd	0.03
9 (CH_3CN)	47.5[i]:2.5	2.5,1.25,1.6	240	0.4	0.2	0.0	0	0	0	nd	--
8[j] (control)	47.5:2.5	2.5,1.25,1.6	185	7.2	3.8	0.002	0.2	trace	3	2.1	<0.01
9 (control)	40:10	0,1.25,1.6	205	--	0	0	0	0	0	nd	--

a. Catalyst: Au/TiO_2 + TS-1, except when noted; 40°C; total pressure: 480 kPa; total flow rate 40 mL/min; 50 mL liquid. All data shown are averages of two or three separate experiments. Data for each row are average of at least two separate experiments.
b. Steady state rates, determined by analysis of composition of gas exiting the reactor.
c. Sum of products formed or reactant consumed over the reaction time indicated, determined from both the gas and liquid phase compositions.
d. Ratio of total epoxide detected to total CO consumed.
e. % by volume, balance He.
f. Only byproduct detected in any significant amount was propanediol in Exp. 1.
g. Total peroxide (H_2O_2 + ROOH), determined by titration analysis of liquid reaction mixture at conclusion of experiment.
h. Methanol solvent was replaced with ethanol.
i. Methanol solvent was replaced with acetonitrile.
j. Catalyst: Au/TiO_2 + silicalite.

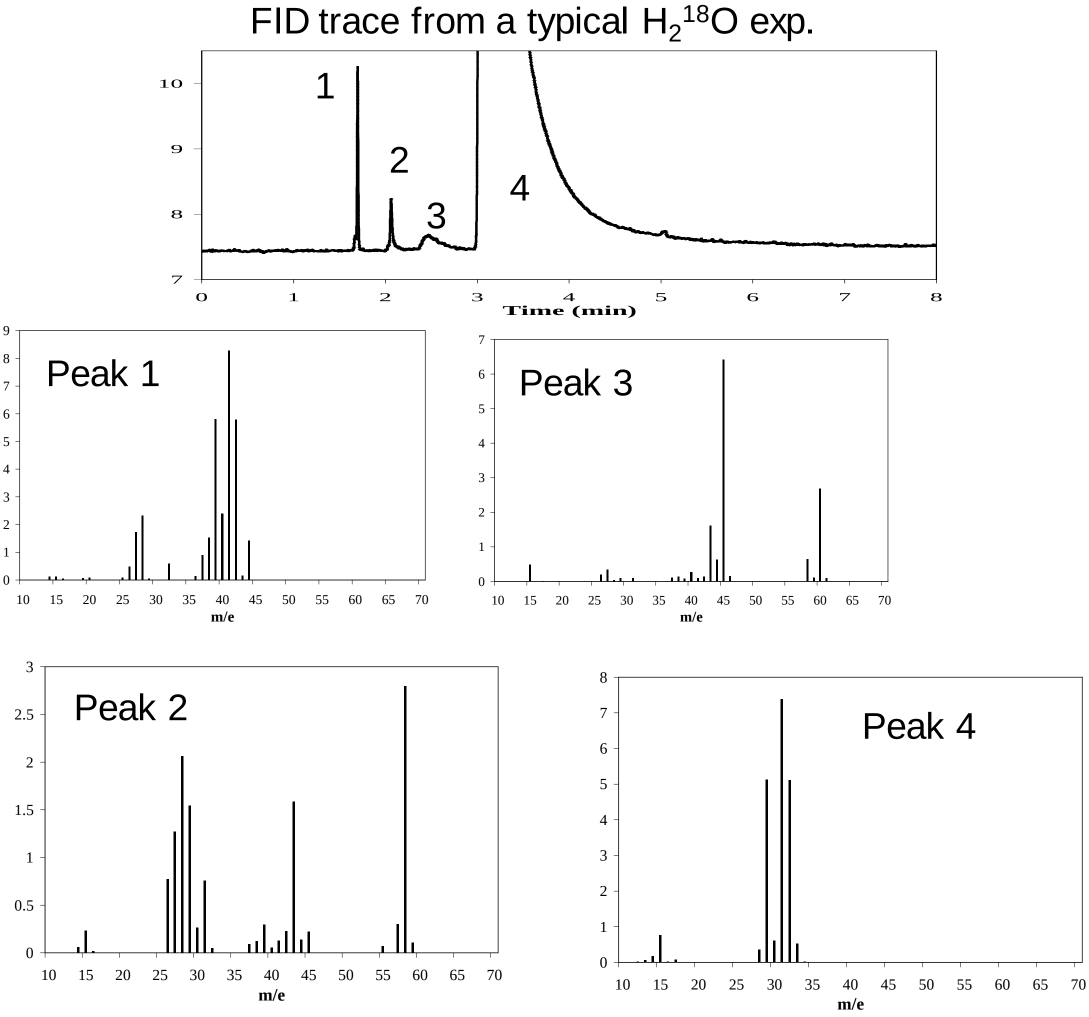

Figure S2. FID trace from a filtered liquid reaction product at the end of a typical experiment with ^{18}O labeled water and methanol (5:95). Reaction conditions: total pressure 480 kPa, temperature 40°C, 40 mL min^{-1} total flowrate, 2.5 % CO, 1.25 % O_2, 1.6% propene, balance He. The MS patterns for the four peaks labeled 1 to 4 are shown below the trace. The pattern for peak 1 matches that of propene (retention time 1.70 min), peak 2 propene oxde-^{16}O (retention time 2.06 min), peak 3 acetone, mostly labeled with ^{18}O (retention time 2.39 min), and peak 4 methanol-^{16}O (retention time 3.15 min).

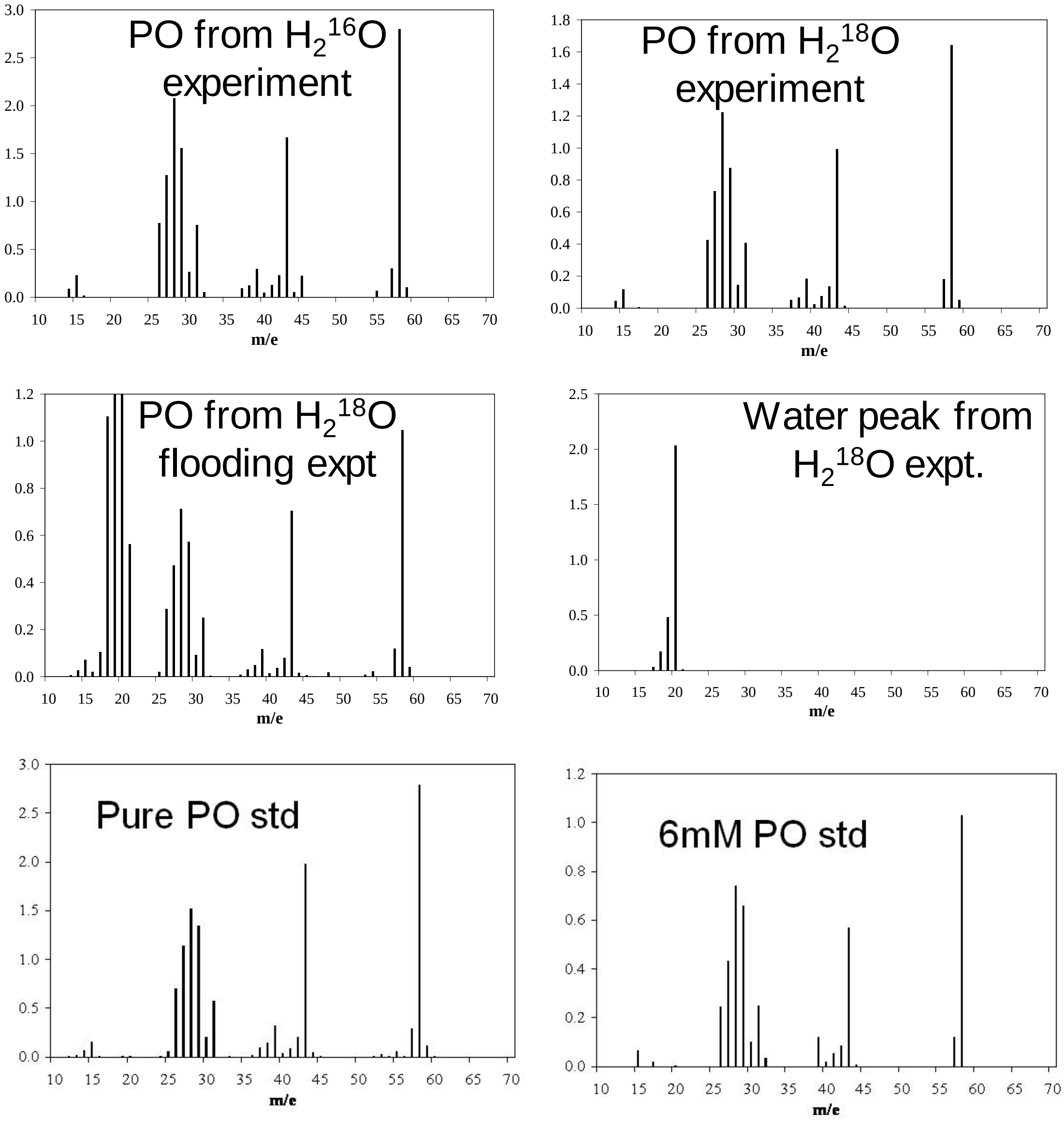

Figure S3. MS patterns of propene oxide from various sources. The top two are PO from experiments using $H_2{}^{16}O$ (left) and $H_2{}^{18}O$ (right). Reaction conditions: 95:5 MeOH:H_2O, total pressure 480 kPa, temperature 40°C, 40 mL min^{-1} total flowrate, 2.5 % CO, 1.25 % O_2, 1.6% propene, balance He. The one labeled "PO from $H_2{}^{18}O$ flooding expt" is the cracking pattern of propene oxide from a solution of propene oxide in ^{18}O labeled water. "Water peak from $H_2{}^{18}O$ exp" is the pattern of the water peak eluted from the GC column, The bottom two patterns are PO standards injected as pure compound (left) of a 6 mM solution in methanol.

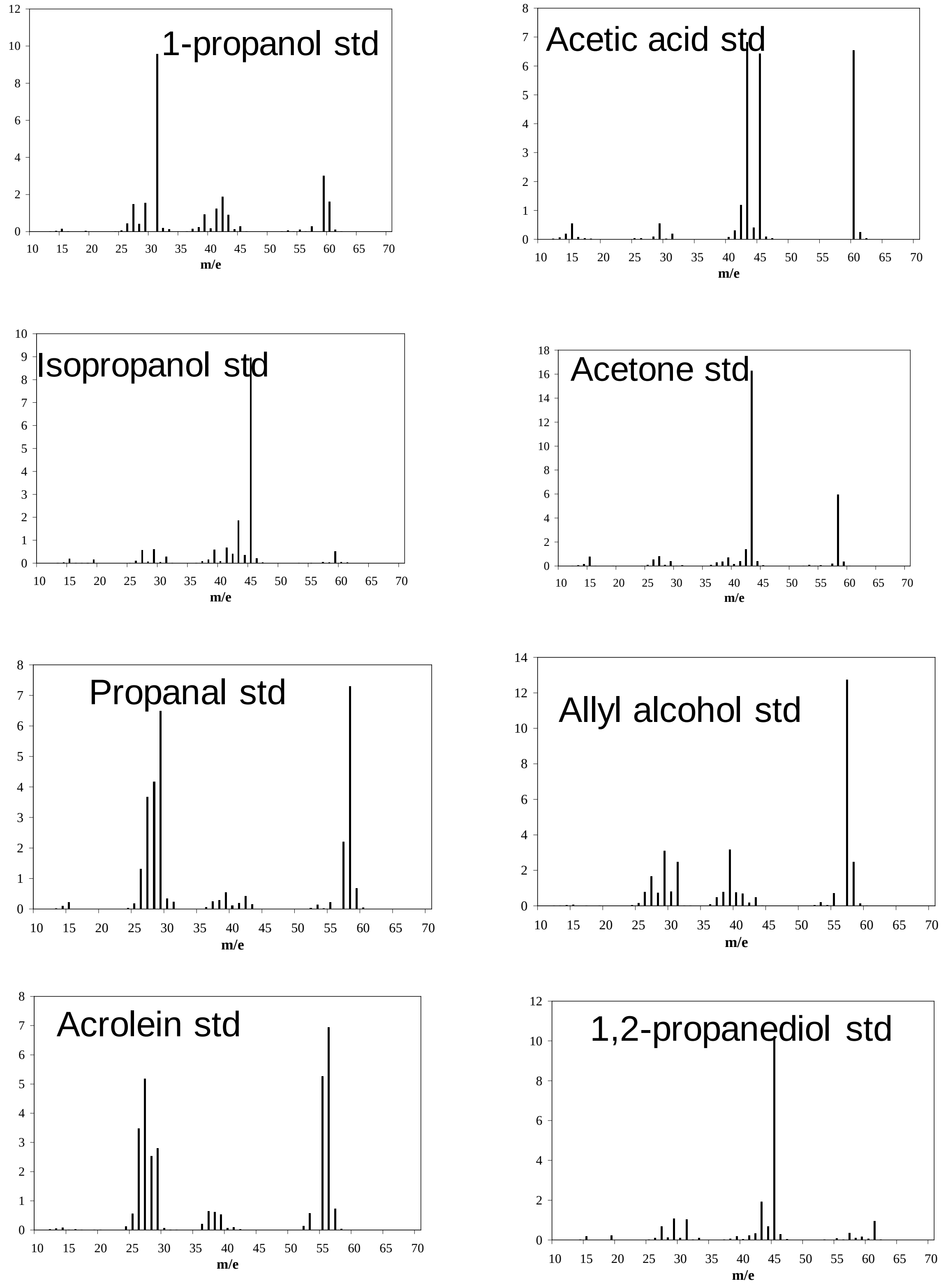

Figure S4. MS patterns of various standards injected as pure compounds into the GC-MS. Their retention times are listed in the Table below.

Table S2. Retention times for various species.

Species	Retention Time (min)
Propene Oxide	2.06
Acetone	2.39
Acetic acid	7.70
1-propanol	4.86
Isopropanol	3.54
1,2-propanediol	8.83
Allyl alcohol	5.58
Propanal	2.23
Acrolein	2.56