Catalytic epoxidation of propene with H_2O-O_2 reactants on Au/TiO$_2$

Manuel Ojeda and Enrique Iglesia*

Dept. of Chemical Engineering, University of California, Berkeley, CA, USA.

Fax: +1 510 642 4778; Tel: +1 510 642 9673; Email: iglesia@berkeley.edu

Products identification by gas chromatography

We used a Porapak-Q packed column (80-100 mesh, 1.82 m x 3.18 mm) connected to a thermal conductivity detector (TCD) and a methyl silicone HP-1 capillary column (50 m x 0.32 mm x 1.05 µm) connected to a flame ionization detector (FID) to analyze products from C_3H_6-O_2-H_2 and C_3H_6-O_2-H_2O mixtures. The reference compounds analyzed in order to assign the GC peaks (FID) were propene (fig. 1), acetone (Fig. 2), propanal (Fig. 3) and propene oxide (Fig. 4). Figure 5 shows an example of a chromatogram of the products of C_3H_6/O_2/H_2O reactions on Au/TiO$_2$.

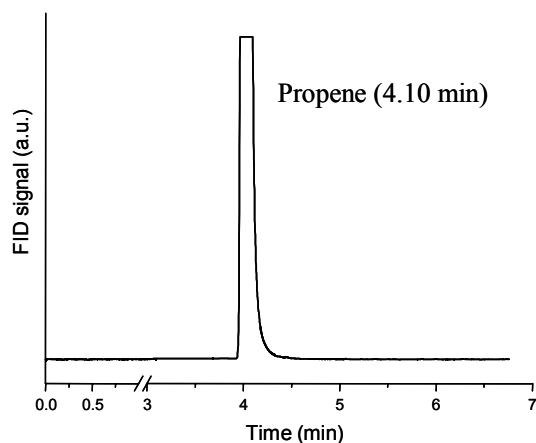Figure 1. Chromatogram of reference propene.
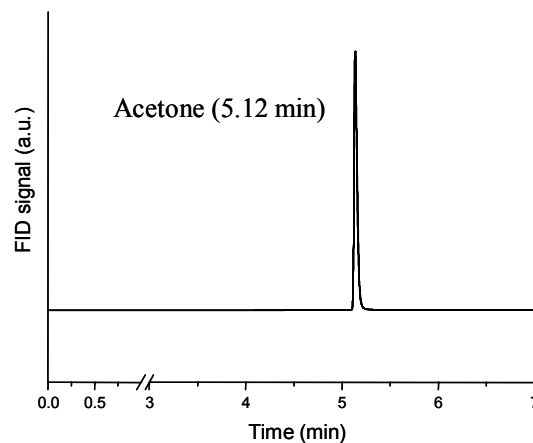

Figure 2. Chromatogram of acetone.
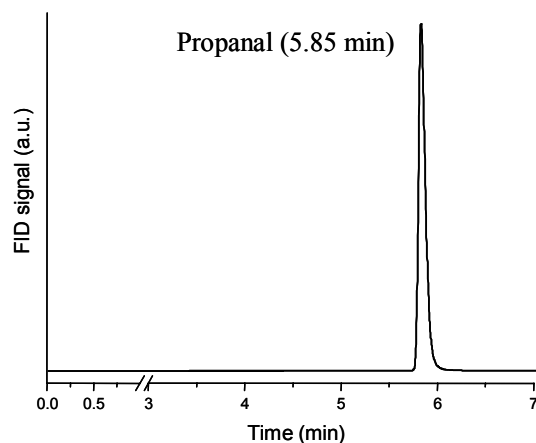

Figure 3. Chromatogram of reference propanal.

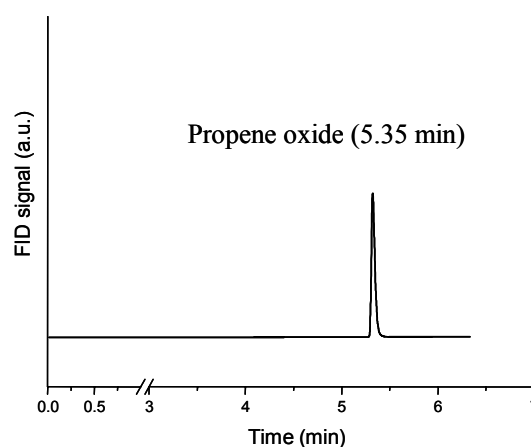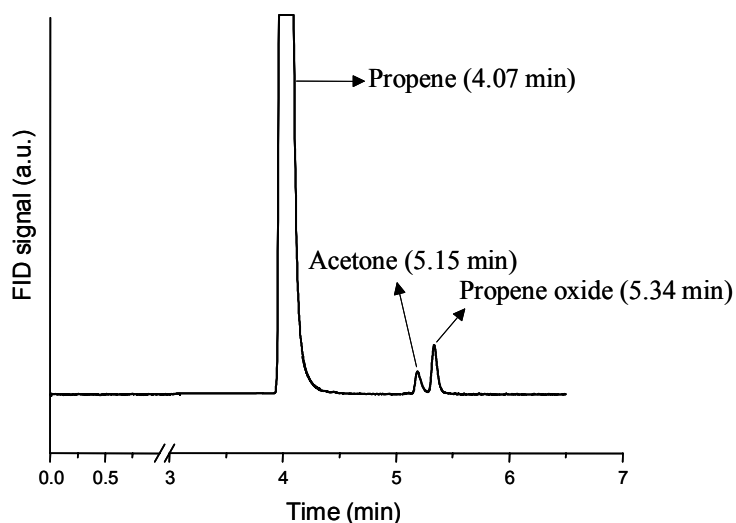Figure 4. Chromatogram of propene oxide.

Figure 5. Chromatogram during C_3H_6/O_2/H_2O reaction on Au/TiO$_2$.

These figures provide evidence for the excellent chromatographic quality and for the accuracy of the peak identification, which was confirmed by their retention times of standard compounds, from which we also obtained the response factors required for quantitation, and also by mass spectrometry. Since propanal (with fragments at amu values common with acrolein) was not detected in the GC as a reaction product, we were able to confirm the absence of acrolein from the lack of intensity at 56 and 57 amu, expected from the NIST mass spectra shown in Figure 6.

Figure 6. MS fragmentation patterns for acrolein (2-propenal) and propanal.
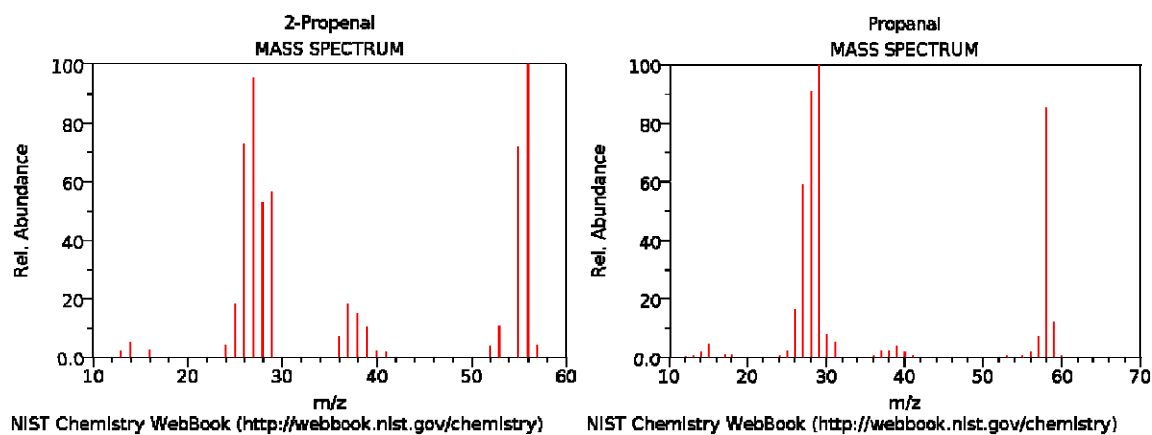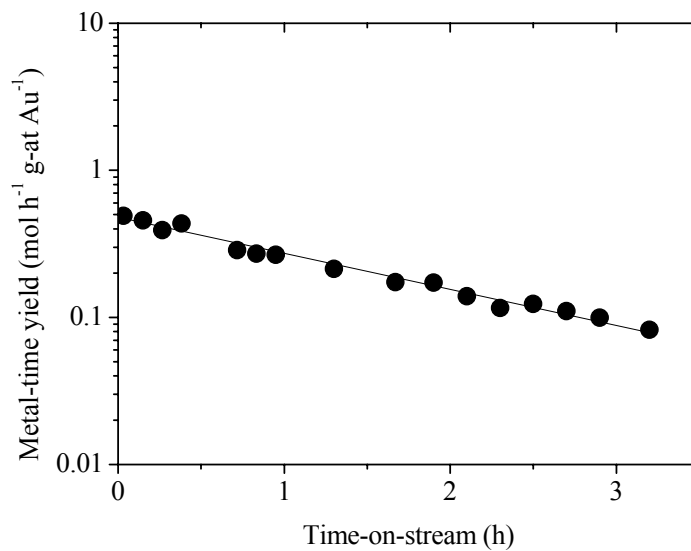
Figure 7. Rate of propylene oxide formation (expressed as metal-time yield) from C_3H_6 (4 kPa) and O_2 (4 kPa) at 350 K from with Au/TiO_2 as a function of time-on-stream using H_2O (2 kPa) as a co-reactant.

Proximity between Au and Ti centers

Au/TiO_2 is widely regarded as a bifunctional catalyst for C_3H_6-O_2-H_2 reaction: Au clusters form hydroperoxy species (HOO*) from H_2 and O_2 that are subsequently transferred to Ti sites, which use these species to epoxidize propene (T.A. Nijhuis et al., J. Catal. 2008, 258, 256 and references herein). Indeed, supported Au catalysts produce hydrogen peroxide from H_2-O_2 mixtures, which is indicative of the formation of HOO* reaction intermediates (G.J. Hutchings and coworkers, Chem. Commun. 2002, 2058), and that Ti-based materials are highly effective in propene epoxidation (M.G. Clerici and coworkers, J. Catal. 1991, 129, 159). Proximity between Au and Ti is a critical role in propene epoxidation from C_3H_6-O_2-H_2 mixtures with Au/TS-1 catalysts (A.M. Joshi *et al.*, J. Phys. Chem. C 2007, 111, 7841 and referenced herein), consistent with the undetectable rates of propene oxide synthesis from C_3H_6-O_2-H_2 or C_3H_6-O_2-H_2O when TiO_2 was present as a physical mixture with Au/Al_2O_3 (lines 17-21; page 1).

Table 1. Propene epoxidation with Au/TiO$_2$ catalysts.

Au size (nm)	Temp. (K)	Reactants	PO rate (mol h^{-1} g-at Au^{-1})	TOF x 10^3 (s^{-1})	Select. (%)	Ref.
3.3	350 K	C$_3$H$_6$/O$_2$/H$_2$/He 4/4/4/88	4.7	5.2	95	This work
3.3	350 K	C$_3$H$_6$/O$_2$/H$_2$O/He 4/4/2/90	0.6	0.7	80	This work
2.4	323 K	C$_3$H$_6$/O$_2$/H$_2$/He 10/10/10/70	3.3	2.2	96	1
-	323 K	C$_3$H$_6$/O$_2$/H$_2$/He 10/10/10/70	4.8	-	99	2
7.2	373 K	C$_3$H$_6$/O$_2$/H$_2$/He 10/10/10/70	1.9	3.8	90	3
2-5	323 K	C$_3$H$_6$/O$_2$/H$_2$/He 10/10/10/70	3.9	2.2-5.4	99	4

1. T. Hayashi, K. Tanaka and M. Haruta, *J. Catal.*, 1998, **178**, 566.

2. T.A.R. Nijhuis, T. Visser and B.M. Weckhuysen, *Angew. Chem. Int. Ed.*, 2005, **44**, 1115.

3. E.E. Stangland, K.B. Stavens, R.P. Andres and W.N. Delgass, *J. Catal.*, 2000, **191**, 332.

4. A.K. Sinha, S. Seelan, S. Tsubota and M. Haruta, *Topics Catal.*, 2004, **29**, 95

Collision rate of H$_2$O$_2$ with Au cluster

The collision rate of H$_2$O$_2$ with the Au clsuters deposited on Au/TiO$_2$ (0.61 wt.%; 3.5 ± 1.2 nm; 152 m^2 g^{-1}) catalyst surface for this pressure has been determined from the Hertz-Knudsen equation:

$$F = \frac{P}{(2\pi m k T)^{1/2}}$$

where F is the flux that strikes the surface, P is the pressure (7×10^{-18} kPa) , m is the mass (5.65×10^{-20} kg), k is the Boltzmann constant (1.3806503×10^{-23} m^2 kg s^{-2} K^{-1}), and T is the temperature (350 K). Substituting: $F \approx 5\times10^{-6}$ mol h^{-1} (g-at Au)$^{-1}$.

High-resolution transmission microscopy (TEM)

Au particle size was determined from TEM micrographs obtained by M. Avalos, L. Rendon and F. Ruiz from the Centro de Ciencias de la Materia Condensada, UNAM, Mexico. TEM analysis was carried out with a JEOL 2010 microscope. Sample preparation involved grinding the catalyst with a mortar and pestle, suspending it in ethanol and depositing a drop of the suspension on a Cu TEM grid. Particle size distribution was obtained by counting between 100 and 300 particles on each sample.

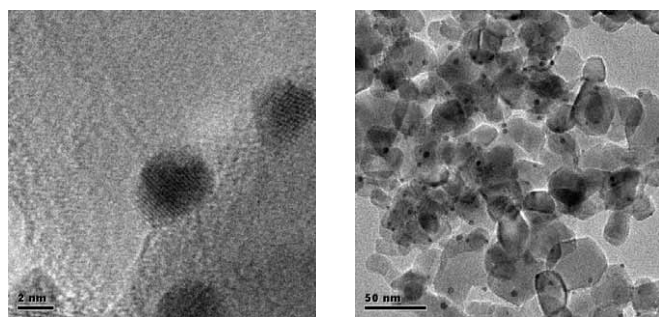Figure 8. Transmission electron micrographs for Au/TiO$_2$ catalyst.

Figure 9. Transmission electron micrographs for Au/Al$_2$O$_3$ catalyst.