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Supplementary Information

Room temperature and atmospheric pressure aqueous partial oxidation of ethane to oxygenates over AuPd catalysts

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Experimental Section

Chemicals

Palladium(II) chloride (≥ 99.9%, $PdCl_2$), Gold(III) chloride trihydrate (≥ 99.9%, $HAuCl_4 \cdot 3H_2O$), Sodium borohydride (99%, $NaBH_4$), Hydrogen peroxide solution (30 wt.%, H_2O_2), Ethanol (reagent grade), Acetaldehyde solution (40 wt.%), Acetic acid (≥ 99.7%), Glycolic acid (99%), Deuterium oxide (99.8 atom% D, D_2O), Phenol (99.0-100.5%), Dimethyl sulfoxide (≥ 99.9%, DMSO), Cerium(IV) sulfate ($Ce(SO_4)_2$) and Hydrochloric acid (37%, HCl) were purchased from Sigma-Aldrich. Formic acid (88%), Ferroin indicator (0.025 M) and Sodium hydroxide (NaOH) were purchased from Fisher Scientific. The 2 mg(Pd)/mL $PdCl_2$ acidic solution was prepared using 0.5 M HCl, and 2 mg(Au)/mL $HAuCl_4$ aqueous solution.

Catalyst Synthesis

AuPd nanoparticles were prepared through a modification of a method reported in the literature.[1] 0.8775 mL $PdCl_2$ acidic solution (2 mg(Pd)/mL) and 1.625 mL $HAuCl_4$ solution (2 mg(Au)/mL) were added to a glass conical flask containing 207.2 mL deionized water. 1.65 mL of freshly prepared $NaBH_4$ aqueous solution (0.1 M) was injected into the solution under stirring (1000 rpm) as two 0.825 mL aliquots. The stirring speed of the produced dark brown colloidal suspension was kept at 1000 rpm for 30 minutes, and then the suspension was boiled vigorously (100 °C) under stirring (1000 rpm) until the suspension volume was between 20 and 25 mL. Of note, continuous stirring is critical to synthesize uniform colloids. After cooling down, the colloidal suspension was made up to 25 mL by adding deionized water. Finally, the as-prepared AuPd colloidal suspension (pH around 2.3) was stored in glass bottle. The suspension was sonicated uniformly prior to use. Au and Pd nanoparticles were prepared using similar processes as for AuPd. To maintain consistency across experiments, Pd nanoparticles were separated by centrifuge and dispersed in HCl aqueous solution (pH around 2.3) prior to use.

Catalyst Testing

A purpose-made PEEK reactor, constructed from Swagelok fittings, was used for all experiments. The reactor has a total volume of 24.5 mL. A Teflon-coated K-type thermocouple was inserted into the reaction liquid to directly measure the reaction temperature. No metal components were in contact with the reaction liquid. For experiments with H_2O_2 oxidant, 5 mL of colloidal catalyst (1 mg AuPd) and a specific amount of H_2O_2 were added to the reactor. Prior to testing, the PEEK reactor was sealed and purged with ethane (99.999%, Matheson) to remove air, and then pressurized with ethane to achieve the desired pressure, typically 1 bar. The reaction liquid was continuously stirred (1000 rpm) at room temperature (21 °C) using a magnetic stirrer for a specific period of time (usually 1 hour). For experiments at elevated temperatures, the reactor was heated and maintained at the desired reaction temperature. After the reaction, the reactor was cooled to a temperature below 15 °C in ice. The headspace gas was extracted using a gas-tight syringe for analysis.

In a typical continuous-feed semi-batch reactor experiment, described in the main text to maintain a low and steady H_2O_2 concentration, catalysts and initial 30 μmol H_2O_2 (10 mM, 3 mL) were added to the reactor (initial 500 μmol acetic acid was added for the corresponding acetic acid oxidation reaction). Then the reactor was connected to a gas-tight syringe pump. Prior to testing, the reactor was purged with ethane (for the ethane oxidation reaction) or nitrogen (for the acetic acid oxidation reaction) for 15 mins. The reactor was then sealed and the pressure was steady at 1 bar.

After 1 h of reaction, 470 µmol H_2O_2 in 2 mL of water was continuously added to the reactor by syringe pump during the following 49 h of reaction time.

Product Analysis

The gas phase products were analyzed by GC (Agilent GC7980) equipped with TCD and FID detectors (Helium as carrier gas). Residual H_2O_2 concentration was determined by titration with acidified $Ce(SO_4)_2$ solution using 8 µL ferroin indicator.[2,3] The liquid phase products were analyzed by 1H-NMR (Bruker 400 MHz NMR) using water suppression technique to decrease the dominant water signal. DMSO (1 mM) and phenol (8 mM) were used as internal standards.[4] Typically, 500 µL liquid product was mixed with 40 µL standards (DMSO and phenol) aqueous solution and 60 µL D_2O for the measurement. The measurements for ethanol, methanol, acetaldehyde, acetic acid, formic acid, and glycolic acid were calibrated from purchased standards following procedures reported in the literature (Figure S2a).[4]

To quantify ethyl hydroperoxide, liquid solutions containing only ethyl hydroperoxide were reduced using prepared fresh 0.05 M $NaBH_4$ solution. After this, the reduced liquid products were analyzed by 1H-NMR. Considering that ethanol was the only reduction product, the amount of ethyl hydroperoxide was related directly to the total amount of ethanol. This procedure was robust and formed the basis of an ethyl hydroperoxide calibration curve (Figure S2b). Notably, considering both ethyl hydroperoxide and ethanol have three peaks located at around 1.07 ppm due to the signal of protons from $C\mathbf{H}_3CH_2$- in 1H NMR spectrum, the areas of the peaks located at 3.96 ppm ($CH_3C\mathbf{H}_2$- of ethyl hydroperoxide) and 3.56 ppm ($CH_3C\mathbf{H}_2$- of ethanol) were calculated to quantify the amount of ethyl hydroperoxide and ethanol, respectively. Methyl hydroperoxide was quantified using analogous methods (Figure S2c).

Catalyst Characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advanced Diffractometer with Cu K_α radiation. X-ray photoelectron spectroscopy (XPS) data were collected on a Thermo ESCALAB 250Xi instrument equipped with a monochromatic Al Kα (hν = 1486.6 eV)) source, and all XPS spectra were calibrated using C 1s peak at 284.8 eV as the reference. ICP-atomic emission spectroscopy (Agilent 725ES) was used for analysis Au/Pd molar ratio. Scanning electron microscopy (SEM) images and electron dispersive X-ray spectroscopy (EDXS) results were obtained on a JSM-5600 LV instrument. Scanning transmission electron microscopy (STEM) images were collected on a JEOL 2100-F-AC operated at 200 kV, and samples were prepared on copper grids coated with ultra-thin holey carbon films.

Computational Methods

Density Funcitonal Theory calculations (as implemented in the Vienna *Ab-initio* Simulation Package)[5] are used to study the C-H bond activation reaction. The AuPd(111) surface is modelled as a four-layer metal slab, consisting of a (4 x 4) fcc unit cells with 19 Å vacuum spacing between the periodic images. All calculations are performed using the RPBE functional[6] with Grimme's D3(BJ)[7] method to account for the dispersion interactions. The transition states are determined using the climbing-image nudged elastic band approach.[8] All calculations use a 400 eV plane-wave cutoff and (3 x 3 x 1) k-point grid. A force threshold of 0.03 eV/Å is used for the geometry optimizations.

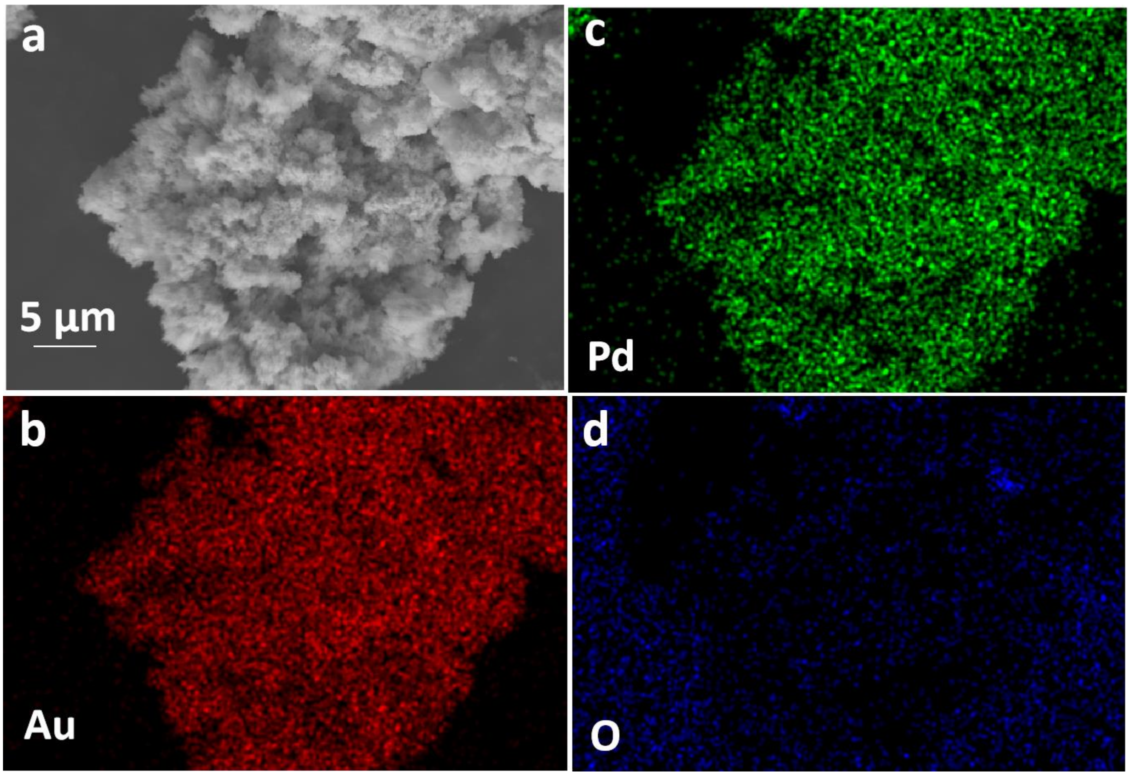

Figure S1. SEM-EDX elemental mapping of AuPd.

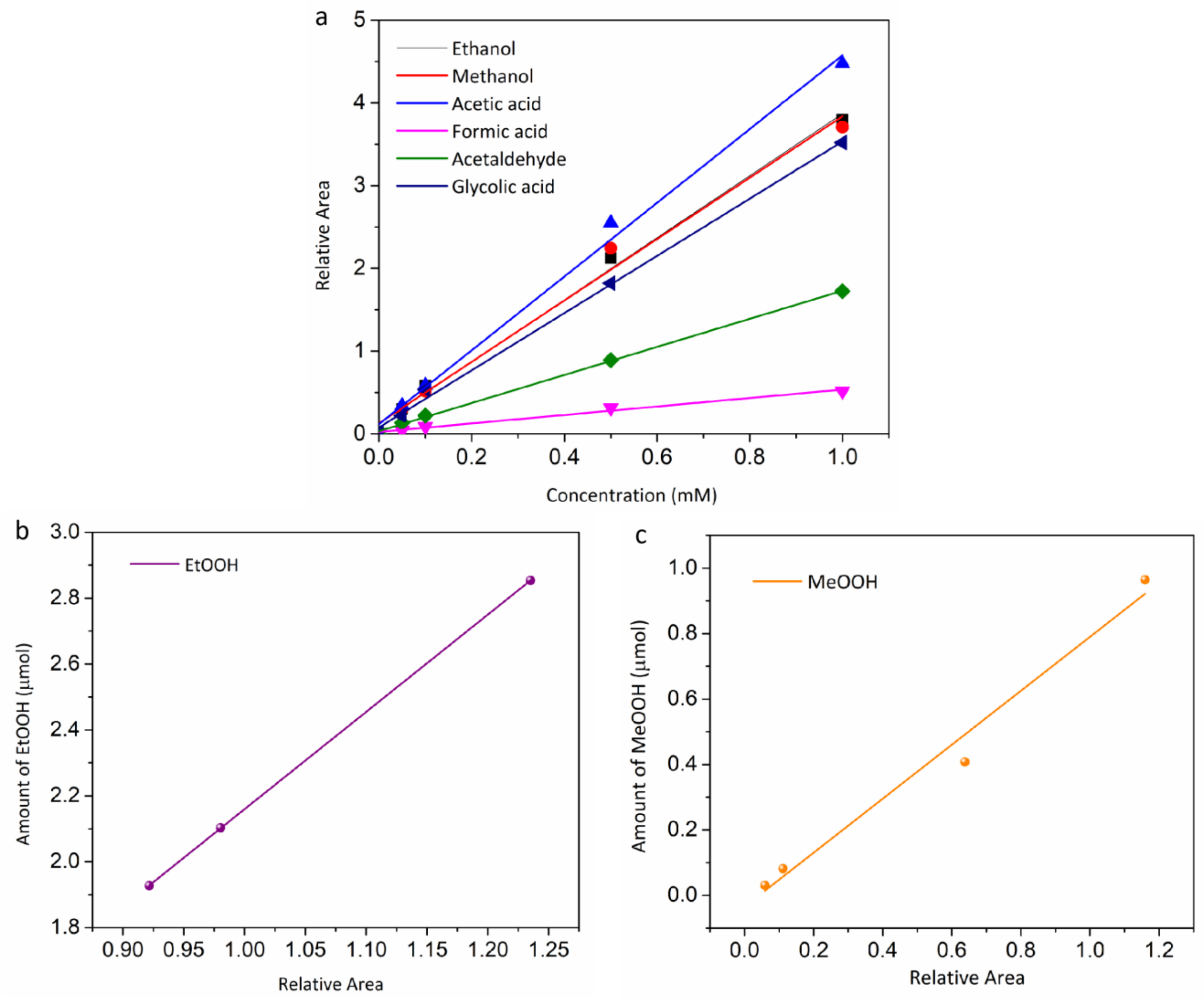

Figure S2. Standard calibration curves for products. (a) Ethanol, methanol, acetaldehyde, acetic acid, formic acid, glycolic acid; (b) ethyl hydroperoxide; (c) methyl hydroperoxide.

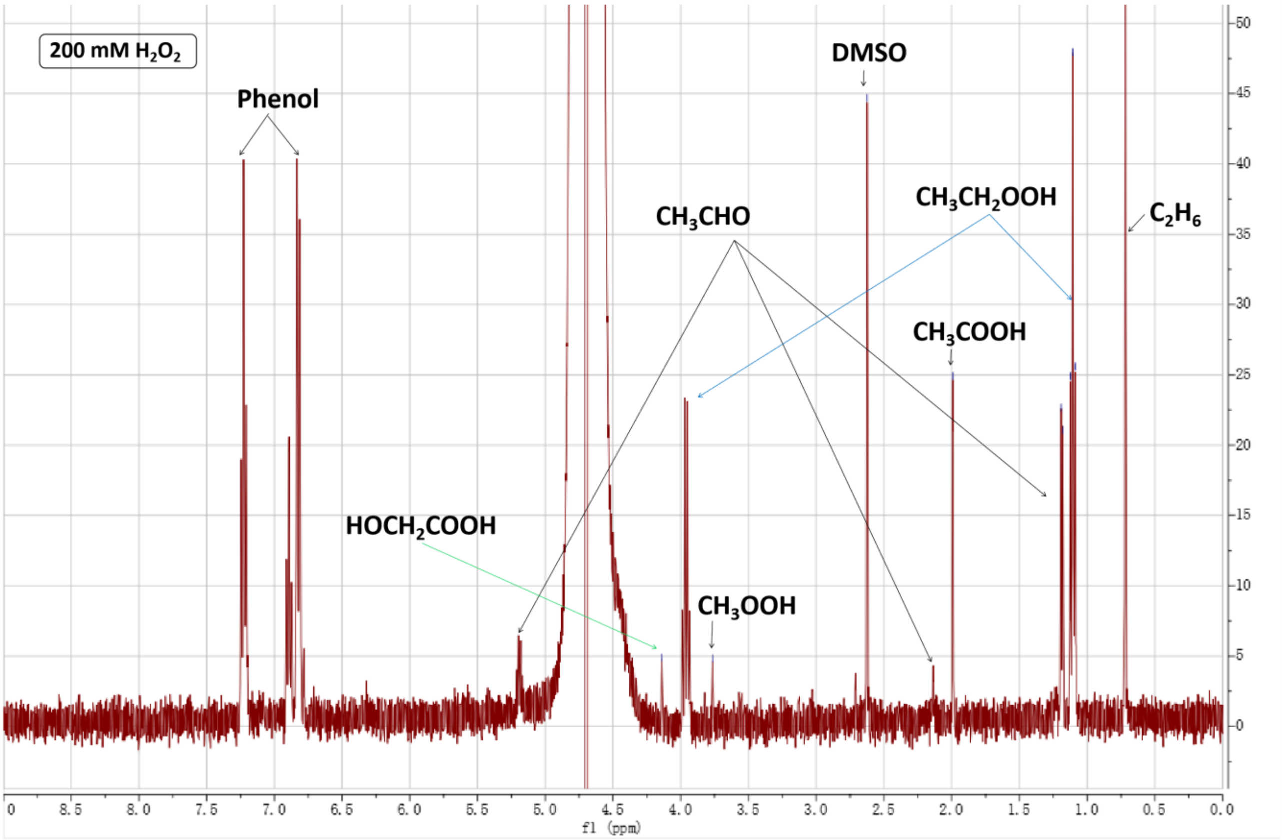

Figure S3. Typical 1H-NMR spectrum for liquid products. This spectrum corresponds to products of the oxidation of C_2H_6 using AuPd with $[H_2O_2]_{initial}$ = 200 mM. Reaction conditions: 5 mL; 1 mg AuPd; 1 bar C_2H_6; 21 °C; 1 h; 1000 rpm.

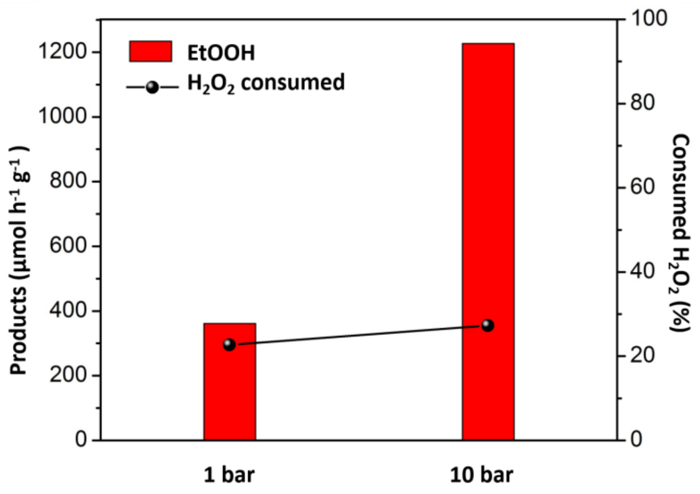

Figure S4. Comparison of catalytic activity of AuPd for C_2H_6 oxidation performed at 1 bar C_2H_6 (Gain factor = 0.0318) and 10 bar C_2H_6 (Gain factor = 0.0899). Gain factor is defined as mol oxygenates/mol H_2O_2 consumed. Reaction conditions: 5 mL; 1 mg AuPd; 1 bar or 10 bar C_2H_6; 21 °C; 1 h; 1000 rpm; $[H_2O_2]_{initial}$ = 10 mM.

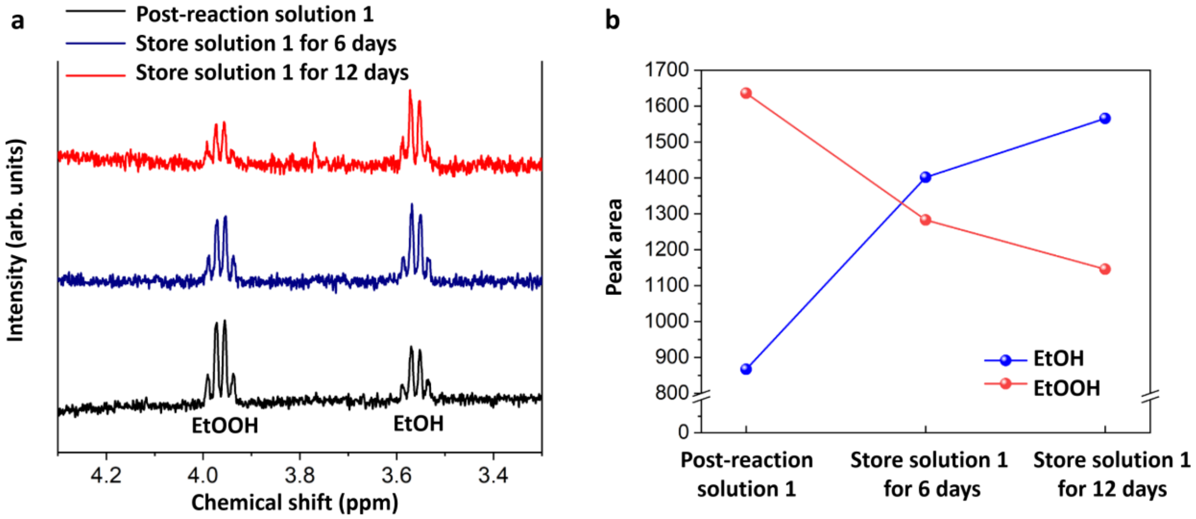

Figure S5. (a) Typical 1H-NMR spectra for low concentrations of liquid products. Solution 1 results from C_2H_6 oxidation over AuPd at 50 °C with 100 mM $[H_2O_2]_{initial}$ for 1 h. (b) Normalized peak areas of EtOOH and EtOH associated with solution 1 after reaction and after storage of the solution for 6 and 12 days. The peak areas of products are normalized to peak area of the internal standard DMSO.

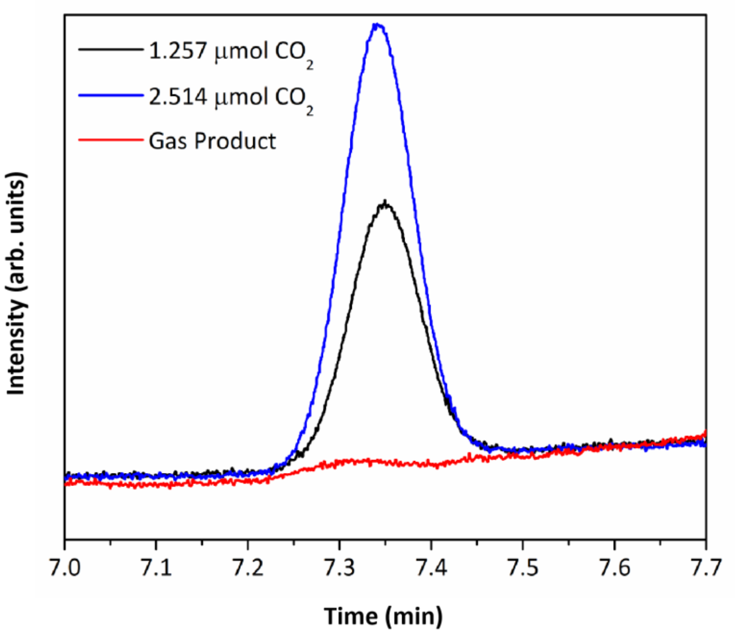

Figure S6. GC curve analyzing CO_2 in the gas phase after reaction over AuPd. CO_2 was nearly undetectable in the gas phase when compared with the calibration results for minute quantities of CO_2.

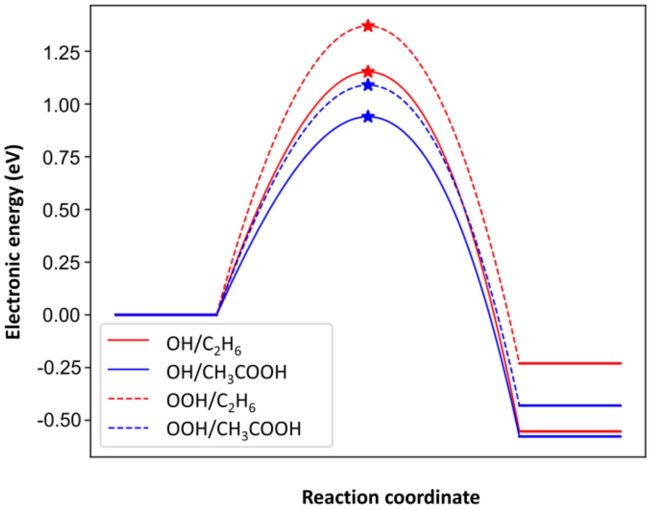

Figure S7. DFT calculations of activation barriers of C_2H_6 and CH_3COOH over AuPd surfaces.

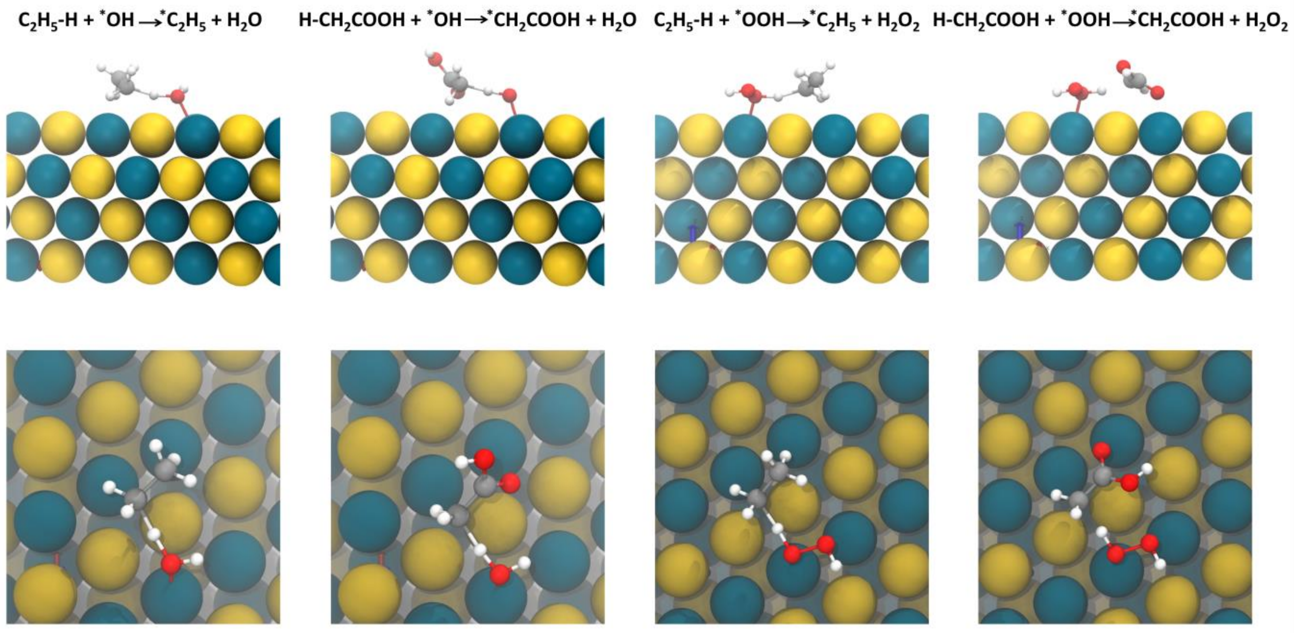

Figure S8. Front and top view for the structures of reaction intermediates and transition states (TS) involved in C_2H_6 and CH_3COOH activation by $^*OH$ and $^*OOH$, respectively, over AuPd surfaces. Yellow: Au; dark green: Pd; gray: C; white: H; red: O.

Table S1. Results of elemental analysis of AuPd.

Elements	EDX[a]				ICP-AES (mg/L)[b]
	Unn. (ωt.%)	Norm. (ωt.%)	Atom. (at.%)	Error (ωt.%)	
O	1.60	2.25	18.07	0.4	n.d.
Pd	23.16	32.48	39.27	0.8	11
Au	46.56	65.28	42.65	1.8	21

	XPS[c]			
Elements	Au	Pd	C	O
Atom. (at.%)	26.26	24.74	20.14	28.86

[a] The Au-Pd molar ratio is determined to be 1.086 by EDX analysis.

[b] The Au-Pd molar ratio is determined to be 1.027 by ICP-AES characterization. n.d. = not determined.

[c] The Au-Pd molar ratio is determined to be 1.061 by XPS analysis.

Table S2. Overview of articles in major journals on heterogeneous ethane oxidation, and associated conditions.

Catalyst	**Reaction conditions[a]**	**Initial H_2O_2 concentration**	**Reference**
AuPd	21 °C and 1 bar	0.001-0.5 M; *In situ* production[b]	This work
Fe- and Cu-containing ZSM-5	50 °C and 5-30 bar	0.1-1 M	*J. Am. Chem. Soc.*, 2013, **135**, 11087–11099
Fe/ZSM-5	30-60 °C and 20 bar; 50 °C and 1-30 bar	0.06-0.3 M	*J. Catal.*, 2015, **330**, 84–92
Fe/ZSM-5	30 °C and 5 bar	0.5 M or 1 M	*Chem. Sci.*, 2014, **5**, 3603–3616
H-ZSM-5	77-120 °C and 30-35.5 bar	0.1-0.4 M	*Appl. Catal. A: General*, 2013, **456**, 82–87
Rh_1O_5/ZSM-5	50-80 °C and 15 bar; 50 °C and 1.5-15 bar	0.5-2.5 M	*ACS Sustainable Chem. Eng.*, 2019, **7**, 4707–4715
TS-1	60 °C and 30 bar	0.116 M	*Tetrahedron Lett.*, 2006, **47**, 3071–3075
Pd/C	70-110 °C and 34.5 bar	*In situ* production	*J. Am. Chem. Soc.*, 1992, **114**, 7308–7310
$(FePc)_2N/SiO_2$; $(FePctBu)_2N/SiO_2$	60 °C and 32 bar	0.339 M	*J. Organomet. Chem.*, 2015, **793**, 139–144

[a] Reaction temperature and initial ethane pressure.

[b] H_2O_2 generated *in situ*.

Table S3. Additional experiments for comparison with AuPd nanoparticle catalysts.[a]

Entry	Catalyst	H_2O_2 amount (µmol)	Products (µmol)			O_2 produced (µmol)	Total liquid products (µmol)	H_2O_2 consumed (%)
			EtOOH	CH_3CHO	CH_3COOH			
1[b]	$PdCl_2/HAuCl_4$	50	0	0	0	0	0	0
2[c]	AuPd	50	0.43	0	0	2.54	0.43	22.2

[a] Reaction conditions: 1 bar C_2H_6; 21 °C; 1 h; 1000 rpm.

[b] Entry 1: Homogeneous metal chloride precursor solutions (3.3 µmol of $PdCl_2$ and 3.3 µmol of $HAuCl_4$ in 5 mL of water).

[c] Entry 2: 5 mL; 1 mg AuPd (6.6 µmol of metals).

Table S4. Comparison of catalytic activity of AuPd catalyst for C_2H_6 oxidation.[a]

Entry	Oxidant	H_2O_2 concentration (mM)	Reaction time (h)	O_2 produced (μmol)[c]	Total liquid products (μmol)	H_2O_2 consumed (μmol)	Gain factor[d]
1	H_2O_2	0	1	0	0	0	0
2	H_2O_2	1	1	n.d.	0.15	2.9	0.0525
3	H_2O_2	10	1	2.54	0.43	11.1	0.0383
4	H_2O_2	30	1	13.27	0.94	95.1	0.0098
5	H_2O_2	100	1	68.55	2.87	318.2	0.0090
6	H_2O_2	200	1	172.19	7.71	663.6	0.0116
7	H_2O_2	500	1	319.45	1.22	1609	0.0008
8	H_2O_2	10	2	5.65	1.26	22.2	0.0569
9	H_2O_2	10	4	5.99	2.06	33.3	0.0619
10	H_2O_2	10	8	10.51	2.83	43.3	0.0654
11[b]	H_2/O_2	n.d.	1	n.d.	4.32	n.d.[e]	n.d.

[a] Typical reaction conditions: 5 mL; 1 mg AuPd; 1 bar C_2H_6 for entries 1 to 10; 21 °C; 1000 rpm. For all entries, CO_2 in the gas phase is in trace amounts (<1 μmol) and could not be quantified by GC-TCD.

[b] $P_{H2} = 0.1$ bar, $P_{N2} = 0.9$ bar, $P_{C2H6} = 1$ bar, $P_{O2} = 0.4$ bar.

[c] The amount of O_2 was determined by GC.

[d] Gain factor is defined as mol of total amount of oxygenates/mol of H_2O_2 consumed.

[e] After reaction, 3.4 μmol H_2O_2 left. n.d. = not determined.

Table S5. Product quantification for C_2H_6 oxidation over AuPd at 50 °C.[a]

Catalyst	H_2O_2 concentration (mM)	Products (µmol)				O_2 produced (µmol)	Total liquid products (µmol)	H_2O_2 consumed (µmol)
		EtOOH	EtOH	CH_3CHO	CH_3COOH			
AuPd	100	2.29	1.13	1.31	0.16	178	4.89	440
AuPd	200	3.00	0.91	2.09	0.29	274	6.29	800
AuPd	500	0.64	0.20	0.57	0.15	792	1.56	2140

[a] Reaction conditions: 5 mL; 1 mg AuPd; 2 bar C_2H_6; 50 °C; 1 h reaction time; 1000 rpm.

Table S6. Comparison of catalytic activity of Pd, Au and AuPd catalysts for ethane oxidation and acetic acid oxidation in semi-batch continuous-H_2O_2-feed reactions.[a]

Entry	Catalyst	Reactant[b]	Conversion (%)[c]	CO_2 produced (µmol)[d]	Total liquid products (µmol)	H_2O_2 consumed (µmol)	Gain factor[e]
1	Pd	CH_3COOH	1.00	3.47	1.54	460	n.d.
2	Au	CH_3COOH	1.22	5.37	0.71	180	n.d.
3	AuPd	CH_3COOH	3.25	12.32	3.91	450	n.d.
4	Pd	C_2H_6	0.58	n.d.[f]	4.63	468	0.0099
5	Au	C_2H_6	0.48	n.d.	3.82	400	0.0096
6	AuPd	C_2H_6	0.82	n.d.	6.51	420	0.0155

[a] Reaction conditions: Pd, Au, or AuPd colloid (6.6 µmol of metals); 1 bar N_2 for entries 1 to 3, and 1 bar C_2H_6 for entries 4 to 6; 21 °C; 50 h; 1000 rpm; 500 µmol H_2O_2.

[b] 500 µmol CH_3COOH or 1 bar C_2H_6 (795 µmol) as reactant.

[c] Conversion = (mol of total amount of oxygenates + mol of CO_2 produced)/mol of reactant in the reactor.

[d] The amount of CO_2 produced was determined by GC.

[e] Gain factor is defined as mol of total amount of oxygenates/mol of H_2O_2 consumed.

[f] For entries 4 to 6, CO_2 in the gas phase is in trace amounts (<1 µmol) and can not be quantified by GC-TCD. n.d. = not determined.

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