Supporting Information

Selective Activation of Propane Using Intermediates Generated during Water Oxidation

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Table S1. Detailed correlation parameters for reaction free energies for reactions:
(1) * + H_2O → *OH + H^+ + e^-,
(2) *OH → *O + H^+ + e^-,
(3) *O + H_2O → *OOH + H^+ + e^-,
(4) *OOH → * + O_2 + H^+ + e^-.
The reaction free energies can be calculated as: ΔG(eV) = αU - 0.0592pH + const.

	Reaction (1)		Reaction (2)		Reaction (3)		Reaction (4)	
	α	const.	α	const.	α	const.	α	const.
Fe@Au	-1.140	0.061	-0.745	0.595	-1.148	2.541	-0.967	1.723
Ir@Au	-0.979	0.149	-0.848	0.768	-1.223	2.147	-0.950	1.856
Mn@Au	-1.035	0.207	-0.745	0.641	-1.101	2.255	-1.120	1.817
Ni@Au	-1.195	0.396	-0.683	0.660	-1.196	2.360	-0.927	1.504
Pd@Au	-1.198	1.033	-0.665	0.752	-1.217	2.225	-0.920	0.909
Ru@Au	-0.993	-0.112	-0.790	0.332	-1.201	2.468	-1.016	2.232
Fe@Ag	-1.019	-0.610	-0.668	0.410	-1.208	2.784	-1.104	2.337
Ir@Ag	-1.034	-0.013	-0.761	0.665	-1.224	2.124	-0.981	2.143
Mn@Ag	-0.882	-0.504	-0.687	0.509	-1.170	2.732	-1.262	2.182
Ni@Ag	-1.011	-0.241	-0.637	0.710	-1.199	2.372	-1.153	2.079
Pd@Ag	-0.971	0.528	-0.614	0.970	-1.251	2.125	-1.165	1.298
Ru@Ag	-1.021	-0.280	-0.800	0.413	-0.859	2.232	-1.320	2.556

Table S2. Reaction free energies for the propane activation by *O (ΔG_{CH}) for zero charge and different potentials. The unit is eV.

SAAs	zero charge	0.00 V_{SHE}	0.50 V_{SHE}	1.00 V_{SHE}	1.23 V_{SHE}	1.50 V_{SHE}
Fe@Au	-0.24	0.07	-0.19	-0.44	-0.56	-0.67
Ir@Au	-0.45	-0.23	-0.41	-0.57	-0.65	-0.74
Mn@Au	-0.19	0.03	-0.16	-0.38	-0.51	-0.60
Ni@Au	-0.35	0.01	-0.29	-0.57	-0.72	-0.84
Pd@Au	-0.44	-0.06	-0.36	-0.72	-0.84	-0.97
Ru@Au	0.14	0.42	0.19	-0.04	-0.15	-0.29
Fe@Ag	0.62	0.58	0.30	0.15	0.14	0.09
Ir@Ag	0.37	0.37	0.26	0.15	-0.04	-0.22
Mn@Ag	0.55	0.52	0.29	0.15	0.14	0.27
Ni@Ag	0.36	0.29	0.03	-0.10	-0.16	-0.33
Pd@Ag	0.21	0.16	-0.10	-0.25	-0.36	-0.46
Ru@Ag	0.72	0.69	0.56	0.44	0.31	0.15

Table S3. Propyl adsorption free energy (*+Pr· → *Pr) (ΔG_{Pr}) for zero charge and different potentials. The unit is eV.

SAAs	zero charge	0.00 V_{SHE}	0.50 V_{SHE}	1.00 V_{SHE}	1.23 V_{SHE}	1.50 V_{SHE}
Fe@Au	0.47	0.62	0.49	0.36	0.31	0.26
Ir@Au	0.54	0.69	0.56	0.44	0.39	0.33
Mn@Au	0.55	0.64	0.55	0.45	0.40	0.40
Ni@Au	0.47	0.63	0.48	0.34	0.29	0.26
Pd@Au	0.49	0.64	0.50	0.33	0.28	0.23
Ru@Au	0.57	0.72	0.57	0.44	0.39	0.33
Fe@Ag	0.97	0.95	0.83	0.83	0.90	0.96
Ir@Ag	1.03	1.02	0.98	0.94	0.87	0.81
Mn@Ag	0.98	0.97	0.92	0.93	1.01	1.17
Ni@Ag	0.99	0.96	0.88	0.92	0.93	0.90
Pd@Ag	1.12	1.09	1.00	1.06	1.05	1.03
Ru@Ag	1.09	1.06	1.01	0.95	0.90	0.84

Table S4. O-H bond formation (*O + H· → *OH) free energy ($\Delta G_{O\text{-}H}$) for zero charge and different potentials. The unit is eV.

SAAs	zero charge	0.00 V_{SHE}	0.50 V_{SHE}	1.00 V_{SHE}	1.23 V_{SHE}	1.50 V_{SHE}
Fe@Au	-3.05	-2.88	-3.01	-3.13	-3.20	-3.27
Ir@Au	-3.17	-3.06	-3.13	-3.20	-3.24	-3.29
Mn@Au	-3.07	-2.94	-3.04	-3.16	-3.24	-3.33
Ni@Au	-3.15	-2.95	-3.10	-3.25	-3.35	-3.42
Pd@Au	-3.26	-3.04	-3.20	-3.38	-3.45	-3.54
Ru@Au	-2.76	-2.63	-2.71	-2.82	-2.88	-2.95
Fe@Ag	-2.68	-2.70	-2.87	-3.02	-3.09	-3.21
Ir@Ag	-3.00	-2.99	-3.05	-3.12	-3.24	-3.36
Mn@Ag	-2.77	-2.78	-2.96	-3.12	-3.21	-3.24
Ni@Ag	-2.97	-3.00	-3.18	-3.35	-3.43	-3.56
Pd@Ag	-3.24	-3.26	-3.44	-3.64	-3.75	-3.83
Ru@Ag	-2.70	-2.70	-2.78	-2.84	-2.93	-3.02

Table S5. Distances between O-H, C-H and C-substrate for the transition state of propane activation and distances between C-substrate in the final state. The unit is Å.

	Transition State			Final State
	O-H	C-H	C-M	C-M
Fe@Au	1.308	1.393	2.431	2.150
Ir@Au	1.277	1.399	2.497	2.154
Mn@Au	1.322	1.385	2.439	2.150
Ni@Au	1.315	1.364	2.472	2.150
Pd@Au	1.318	1.353	2.531	2.153
Ru@Au	1.235	1.440	2.522	2.156
Fe@Ag	1.194	1.475	2.426	2.213
Ir@Ag	1.195	1.462	2.502	2.225
Mn@Ag	1.217	1.450	2.445	2.217
Ni@Ag	1.233	1.403	2.495	2.206
Pd@Ag	1.257	1.398	2.509	2.217
Ru@Ag	1.159	1.532	2.443	2.220

Table S6. Free energy barriers for C-H cleavage obtained from single point energy (SPE) and energies from structural optimization (OPT). The unit is eV.

SAAs	zero charge	0.00 V_{SHE}	0.50 V_{SHE}	1.00 V_{SHE}	1.23 V_{SHE}	1.50 V_{SHE}
SPE	0.73	0.89	0.78	0.69	0.62	0.57
OPT	0.73	0.90	0.78	0.69	0.62	0.57

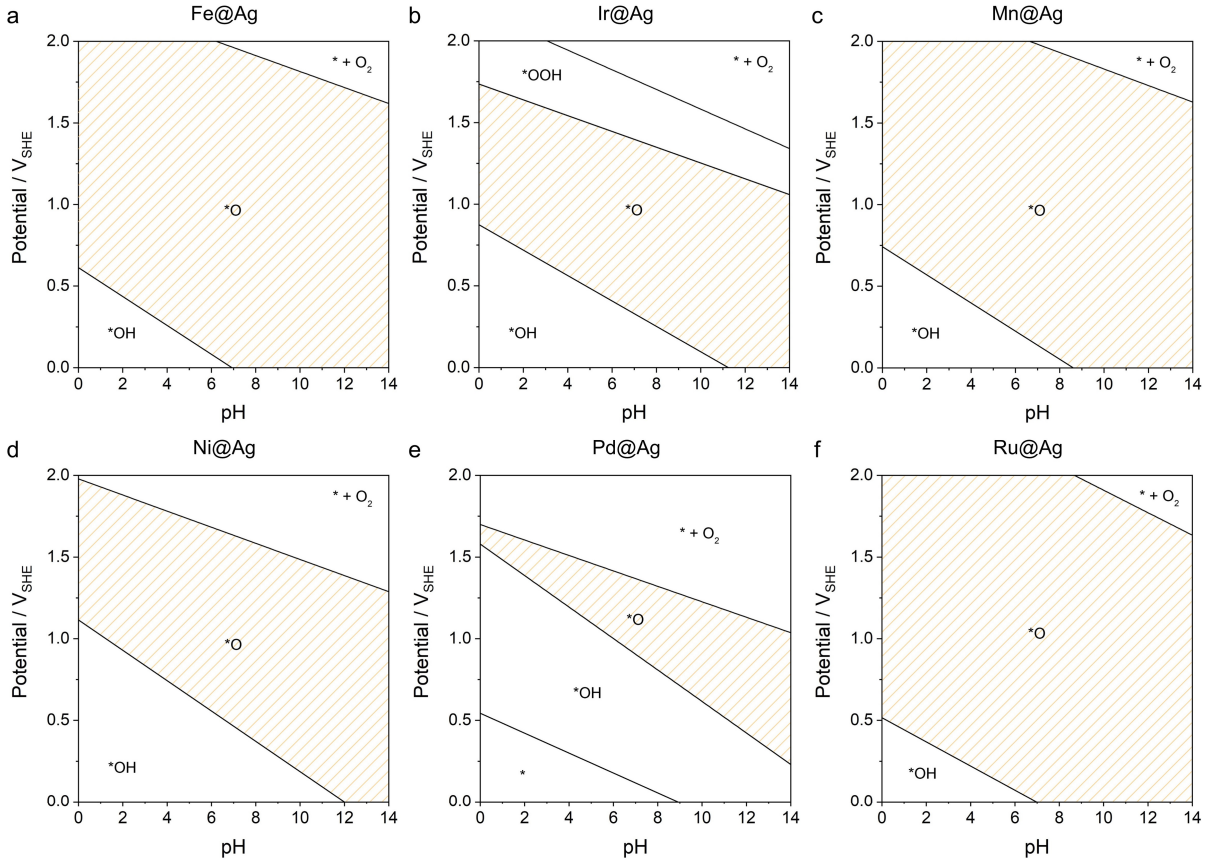

Figure S1. Surface Pourbaix diagram for Ag-based SAAs. Shaded area indicates the pH and potential range at which *O will exist.

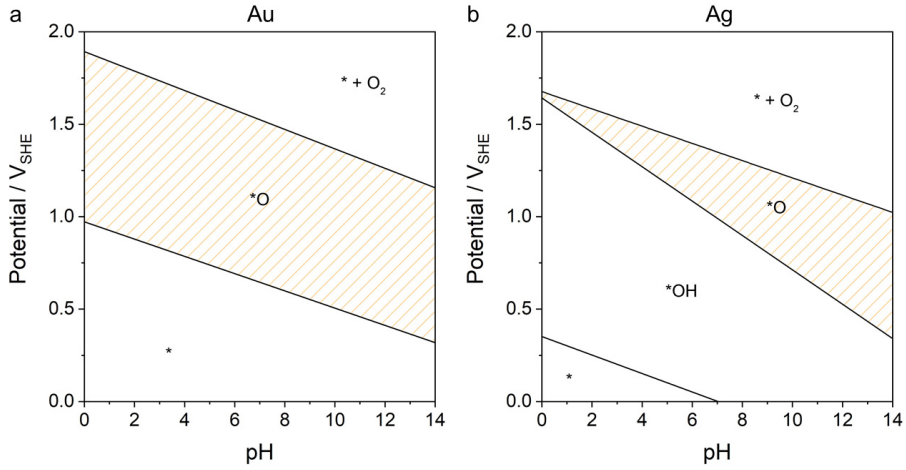

Figure S2. Surface Pourbaix diagrams for pristine Au (**a**) and Ag (**b**) surfaces.

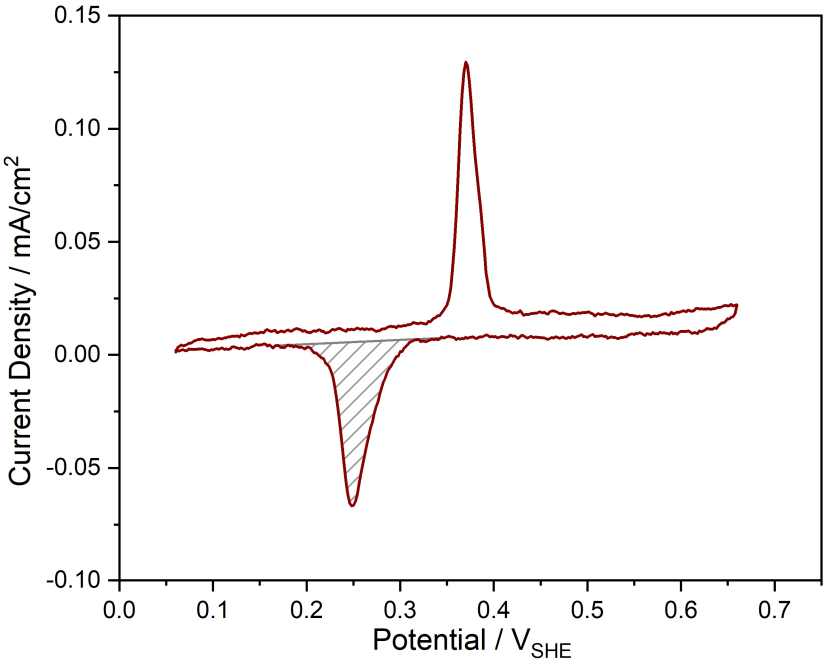

Figure S3. Cyclic voltammetry profile for under potential deposition of Ni on Au. A pair of cathodic and anodic peaks is observed in the UPD range, at 0.25 and 0.37 V_{SHE}, respectively. The electric charge for Ni deposition is calculated to be ~584 $\mu C/cm^2$ based on the shaded area in the cathodic scan with a scan rate of 20 mV/s. In principle, approximately 596 $\mu C/cm^2$ is required to achieve a mono-layer coverage of close-packing Ni on Au surface.

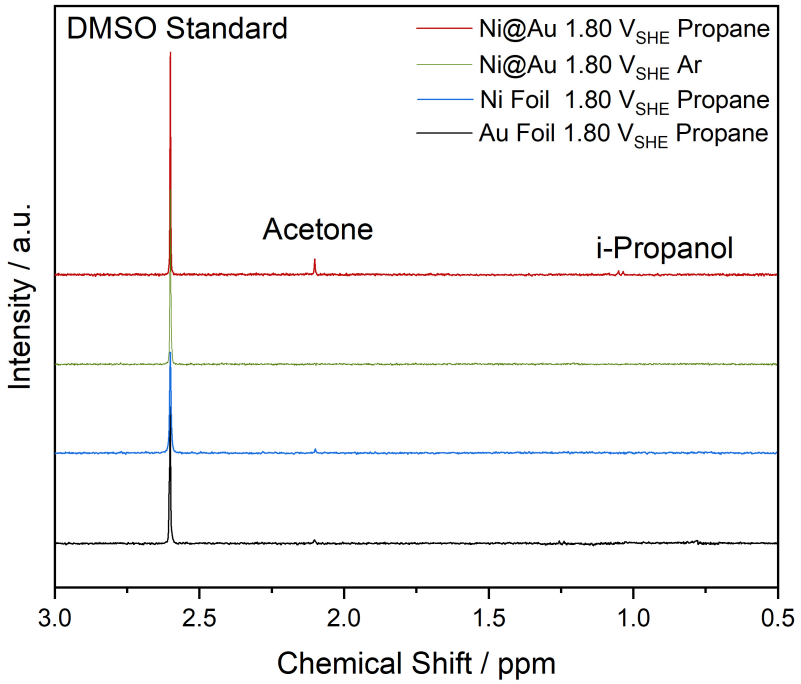

Figure S4. NMR spectra of the electrolytes using Ni@Au, pristine Au and Ni as the catalyst for propane electrolysis. NMR spectrum of the control experiment under Ar atmosphere on Ni@Au is provided. All spectra are scaled such that the areas of the internal standard (DMSO) are the same. Pristine Au and Ni foil produces significantly less acetone with identical conditions.