Supporting Information

Descriptor-based Identification of Bimetallic-derived Catalysts

for Selective Activation of Ethane with CO_2

Haoyue Guo,^{†#} Zhenhua Xie,^{†‡#} Xuelong Wang,[†] Jingguang G. Chen,^{†‡*} and Ping Liu^{†*}

† Chemistry Division, Brookhaven National Laboratory, Upton, NY 11973

‡ Department of Chemical Engineering, Columbia University, New York, NY 10027



Figure S1. The Fourier-transformed EXAFS (FT-EXAFS) spectra of $PtIn_3/CeO_2$ under different conditions and corresponding fitting plots in the R space. The fresh sample (He@298 K) was subsequently exposed to the conditions of "H₂@723 K", "He 823 K" and "Rxn@823 K" (i.e., $CO_2+C_2H_6@823$ K). (a) In K-edge; (b) Pt L₃-edge. Model compounds used for the EXAFS fittings: In K-edge—In₂O₃, Pt₃In, In; Pt L₃-edge—PtO₂, Pt₃In, Pt, CeO₂.



Figure S2. The FT-EXAFS spectra of RhIn₃/CeO₂ under the reaction condition and corresponding fitting plots in the R space. "Rxn@823 K" referred to that the reaction was carried out with both CO₂ and C₂H₆ at 823 K. (a) In K-edge; (b) Rh K-edge. Model compounds used for the EXAFS fittings: In K-edge—In₂O₃, Rh₃In and RhIn₃; Rh K-edge—Rh₃In and Rh.



Figure S3. Configurational variations with two-dimensional descriptors: formation energy of alloy surface and the reactive oxygen binding energy on InM₃, In₃M and PdM₃¹ catalysts (left/right semi-circle: thermodynamically preferred surface configuration before/under reaction).

The DFT calculations were performed on AB₃ bimetallic systems to first map the stable surface phases before and under reactions, and on the basis screen the catalysts for selective activation of ethane and CO₂ using the descriptors identified in our previous study: formation energies of alloy surfaces and the reactive oxygen binding energies¹. Among the systems studied, most of the bare bimetallic surfaces maintain the bulk-terminated AB₃(111) configuration (green cycles, **Figure S3**), *e.g.*, Ni₃In, Rh₃In, Pt₃In; while the skinned conformation is more stable when component A prefers to segregate, *e.g.*, PdFe₃, PdRu₃, PdRh₃ (blue cycles, **Figure S3**), and the sandwich model is favored with the segregation of B, *e.g.*, NiIn₃, RhIn₃, PtIn₃ (red cycles, **Figure S3**), depending on the relative stability of two components on the surface. Under reaction conditions, where the chemisorbed *O formed from CO₂ dissociation, the preferred surface conformation depends on

the competition between the oxygen binding energy and the formation energy of alloy surface. For alloy surfaces with negative formation energy (< -0.5 eV) and thus high stability, *e.g.*, Rh₃In, Pd₃In, Pt₃In, the bulk-terminated mixed alloy surfaces seem to remain, despite that the corresponding binding to *O is relatively strong, *e.g.*, Rh₃In or weak, *e.g.*, Pd₃In, Pt₃In (one kind of color in a circle, **Figure S3**). By comparison, the oxygen-driven surface segregation emerges for the systems with less negative, *e.g.*, RhIn₃, or positive formation energy, *e.g.*, Ru₃In, (> -0.5eV) and thus lower stability (two kinds of color in a circle, **Figure S3**). In both cases, the strong oxygen binding can drive the surface segregation going from the bulk-terminated alloy surfaces to skin or sandwich surfaces and thus the oxidation of surface metal atoms, *e.g.*, PdAg₃, PdAu₃. Or it leads to the direct oxidation of surface if the skin or sandwich structures are preferred for bare surfaces, *e.g.*, PtSn₃, PtIn₃. In both cases the formation of oxide/metal interfaces is observed¹⁻⁴. The difference in phase preference between metal/oxide interfaces and metal surfaces under reaction conditions have been previously reported to provide distinct activity and selectivity^{4, 5}.



Figure S4. DFT optimized structures (top views) of (a) In_2O_4 , (b) In_2O_5 , (c) In_2O_6 with the sixth *O at the In-In bridge site, (d) In_2O_6 with the sixth *O at the *hcp* hollow site, (e) In_2O_6 with the sixth *O at the interfacial *fcc* hollow site, (f) In_2O_7 cluster on Rh(111) surface with the formation energies underneath (Rh: ivory; In: pink; O: red).



Figure S5. DFT optimized structures (top views) of (a) collapsed In_2O_5 , (b) In_2O_5 with the fifth *O at the In-In bridge site, (c) In_2O_6 with the sixth *O at the *hcp* hollow site, (d) In_2O_6 with the sixth *O at the *fcc* hollow site, (e) In_2O_7 with the seventh *O at the *hcp* hollow site, (f) In_2O_8 with the seventh *O at the interfacial *fcc* hollow site on Pt(111) surface with the formation energies underneath (Pt: gray; In: pink; O: red).



Figure S6. The DFT-optimized structures of the intermediates on In₂O₅/Rh(111) surface. Top

image (side view) and bottom image (top view) of (a) *O, (b) *CH₃CH₂+*O, (c) *CH₂CH₂+*O,
(d) *CH₃CH₂O, (e) *CH₃CHO, (f) *CH₃CO, (g) *CH₃, (h) *CO (Rh: ivory; In: pink; O: red; C: brown; H: white).



Figure S7. The DFT-optimized structures of the intermediates on In₂O₇/Pt(111) surface. Top image (side view) and bottom image (top view) of (a) *O, (b) *CH₃CH₂+*O, (c) *CH₂CH₂+*O, (d) *CH₃CH₂O, (e) *CH₃CHO, (f) *CH₃CO, (g) *CH₃, (h) *CO (Pt: gray; In: pink; O: red; C: brown; H: white).



Figure S8. The DFT-optimized structures of (a) *CH₃CH₂ and (b) *CH₃CH₂O on Fe₃O₃/Ni(111), (c) *CH₃CH₂ and (d) *CH₃CH₂O on Fe₃O₇/Ni(111) (Fe: yellow; Ni: silver; O: red; C: brown; H: white).



Figure S9. The DFT-optimized structures of (a) *CH₃CH₂ and (b) *CH₃CH₂O on Fe₃O₃/Pd(111), (c) *CH₃CH₂+*O and (d) *CH₃CH₂O on Fe₃O₆/Pd(111) (Fe: yellow; Pd: gray; O: red; C: brown; H: white).



Figure S10. The DFT-optimized structures of (a) $*CH_3CH_2$ and (b) $*CH_3CH_2O$ on $Ga_2O_5/Pd(111)$, (c) $*CH_3CH_2+*O$ and (d) $*CH_3CH_2O$ on $Ga_2O_7/Pd(111)$ (Ga: green; Pd: gray; O: red; C: brown; H: white).

Samples	Conditions	Shell	CN	Bond length (Å)	σ^2 (Å ²)	E ₀ shift (eV)	R factor
PtIn ₃ /CeO ₂ ^a	He@298K	In-O	6.1(1)	2.15(0)	0.008	3.35	0.014
(In K-edge)		In-In*	1.9(3)	3.37(1)	6 0.008 6	3.35	
	H ₂ @723K	In-O	2.5(1)	2.12(0)	0.010	3.65	
		In-Pt	1.4(3)	2.66(1)	0.010 6	4.60	
		In-In	0.48(32)	3.40(5)	0.010	4.60	
	He@823K	In-O	2.1(1)	2.11(0)	0.011 7	2.46	
		In-Pt	1.0(1)	2.67(1)	0.007	5.66	
		In-In	0.82(16)	3.48(1)	0.007 0	5.66	
	$CO_2+C_2H_6$	In-O	2.7(1)	2.14(0)	0.012	5.58	
	@823K	In-Pt	1.6(3)	2.66(1)	0.011 6	5.23	
		In-In	0.50(42)	3.56(6)	0.011	5.23	
PtIn ₃ /CeO ₂ ^b (Pt L ₃ -edge)	He@298K	Pt-O	5.1(1)	2.00(0)	0.001 1	12.58	0.010
	H ₂ @723K	Pt-Pt*	1.9(4)	3.14(1)	0.001 1	12.58	
		Pt-In	2.1(1)	2.62(0)	0.005 3	1.88	
		Pt-Pt	2.8(2)	2.73(1)	0.005 3	1.88	
		Pt-Pt**/Ce	0.93(27)	3.84(2)	0.005 3	1.88	
	He@823K	Pt-In	2.1(1)	2.64(0)	0.004 4	2.38	
		Pt-Pt	2.8(2)	2.74(1)	0.004 4	2.38	
		Pt-Pt**/Ce	0.64(31)	3.86(3)	0.004 4	2.38	
	CO ₂ +C ₂ H ₆ @823K	Pt-In	2.0(1)	2.64(1)	0.005 7	2.12	
		Pt-Pt	3.2(3)	2.75(1)	0.005 7	2.12	
		Pt-Pt**/Ce	1.14(38)	3.87(2)	0.005 7	2.12	
RhIn ₃ /CeO ₂ (In K-edge)	$CO_2+C_2H_6$ @823K	In-O	1.4(0)	2.14(0)	0.003 5	9.34	0.014

 Table S1 Fitting results of the *in situ* FT-EXAFS spectra of the PtIn₃/CeO₂ and RhIn₃/CeO₂

 catalysts under different conditions.

		In-Rh	0.55(3)	2.59(0)	0.000	2.42	
		In-Rh**	0.61(3)	2.79(0)	0.000	13.8	
RhIn ₃ /CeO ₂ (Rh K-edge)	CO ₂ +C ₂ H ₆ @823K	Rh-In	2.9(3)	2.57(1)	0.003	-2.8	
		Rh-Rh(In)	3.6(3)	2.75(1)	3 0.003	-4.9	
		Rh-Rh**	2.2(8)	3.54(3)	3 0.009	-1.99	
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Notes: CN—average coordination number (normalized to all the absorbers) around the absorbing center atom; σ^2 —mean square variation in path length; R-factor—quality of fitting.

^a: $\Delta k=2-11$ Å⁻¹, $\Delta R=1.0-3.5$ Å, $k^1k^2k^3$ -weighted EXAFS fitting;

^b: Δk =3-11 Å⁻¹, ΔR =1.3(5)-4.0 Å, k¹k²k³-weighted EXAFS fitting;

°: Δk =2-10 Å⁻¹, ΔR =1.2-4.0 Å, k¹k²k³-weighted EXAFS fitting;

^d: $\Delta k=2-10$ Å⁻¹, $\Delta R=1.5-4.0$ Å, $k^1k^2k^3$ -weighted EXAFS fitting;

"*" referred to the metal-oxygen-metal scattering path in the metal oxide;

"**" referred to the longer metal-metal bonds

The number in the parentheses referred to the uncertainty of the last one (or two) digit(s) after the decimal.

Table	S2 .	Comparison	of	binding	energies	of	reaction	intermediates	on	$In_2O_5/Rh(111)$	and

 $In_2O_7/Pt(111).$

Adsorbates	Bound via	$E_{\rm b}$ (eV) In O /Rh(111)	$E_{\rm b}$ (eV) In O /Pt(111)		
*0	0	-1.72	-0.86		
*OH	0	-2.59	-2.96		
*CH ₃ CH ₂ O	0	-1.82	-0.69		
*CH ₃ CHO	С, О	-0.18	-0.15		
*CH ₃ CO	С	-2.38	-1.96		
*CH ₃	С	-1.75	-1.98		
*CO	С	-1.95	-1.56		
*CH ₃ CH ₂	С	-1.31	-1.51		
*CH ₂ CH ₂	C, C	-0.81	-1.08		

References:

- 1. Z. Xie, X. Wang, X. Chen, P. Liu and J. G. Chen, J. Am. Chem. Soc., 2022, 144, 4186-4195.
- 2. B. Yan, S. Yao, S. Kattel, Q. Wu, Z. Xie, E. Gomez, P. Liu, D. Su and J. G. Chen, *Proc. Natl. Acad. Sci. U.S.A.*, 2018, **115**, 8278-8283.
- 3. Z. Xie, D. Tian, M. Xie, S.-Z. Yang, Y. Xu, N. Rui, J. H. Lee, S. D. Senanayake, K. Li, H. Wang, S. Kattel and J. G. Chen, *Chem*, 2020, **6**, 2703-2716.
- 4. E. Gomez, S. Kattel, B. Yan, S. Yao, P. Liu and J. G. Chen, *Nat. Commun.*, 2018, 9, 1398.
- 5. Z. Xie, L. R. Winter and J. G. Chen, *Matter*, 2021, 4, 408-440.