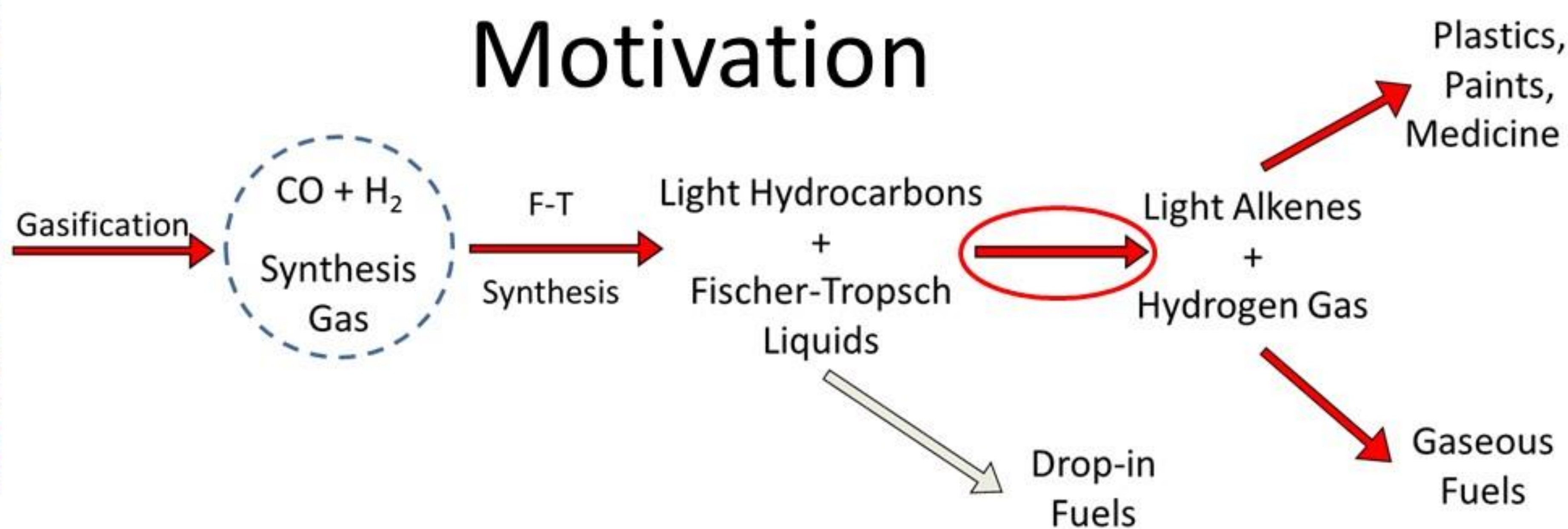
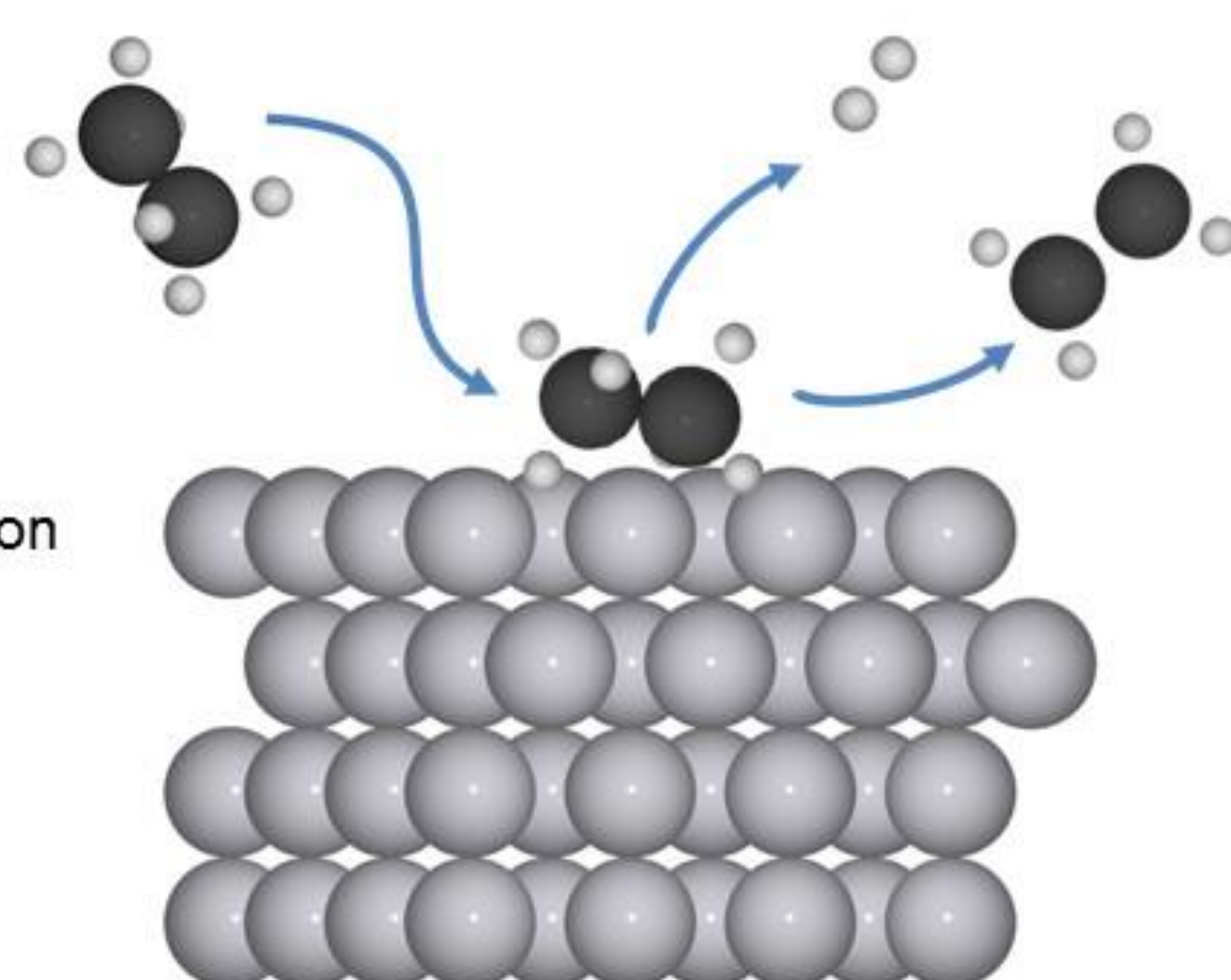




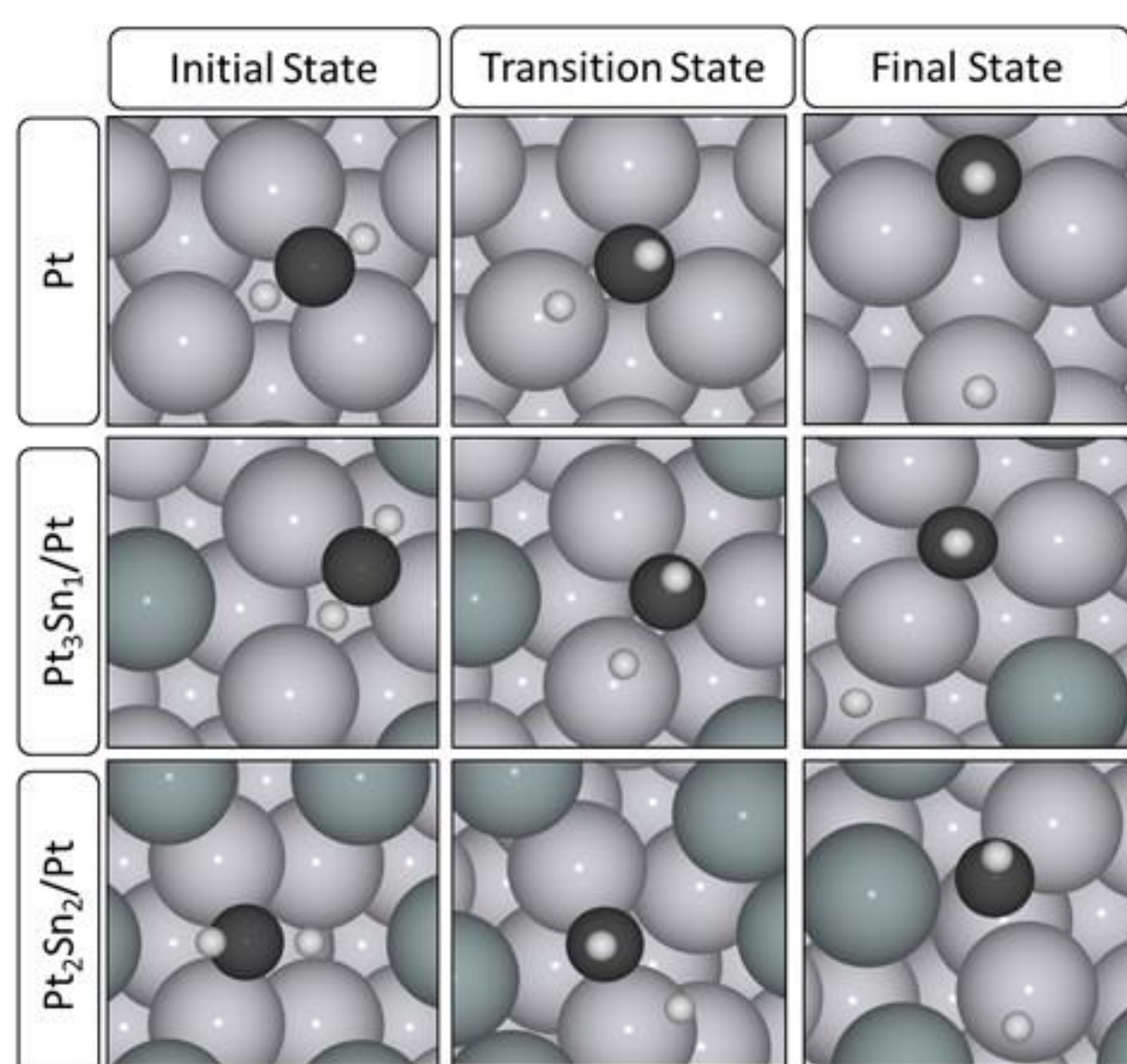
Motivation



- Light Alkanes are cheap and abundant
 - Methane is commonly flared, Ethane is flared in some areas
- Dehydrogenation to ethylene greatly increases value
- Platinum is highly active in light alkane dehydrogenation
 - High requisite temperature causes coke formation leading to catalyst deactivation
 - Alloying platinum with tin is known to suppress coke
 - Mechanism for coke formation is not well understood
- Objectives:
 - Investigate effects of platinum tin alloy structure and composition on the kinetics and thermodynamics of light alkane dehydrogenation
 - Better understand how tin suppresses coke formation
 - Explore possible coke forming mechanisms
 - Compare ethylene selectivity verses coke



Single Carbon Kinetics

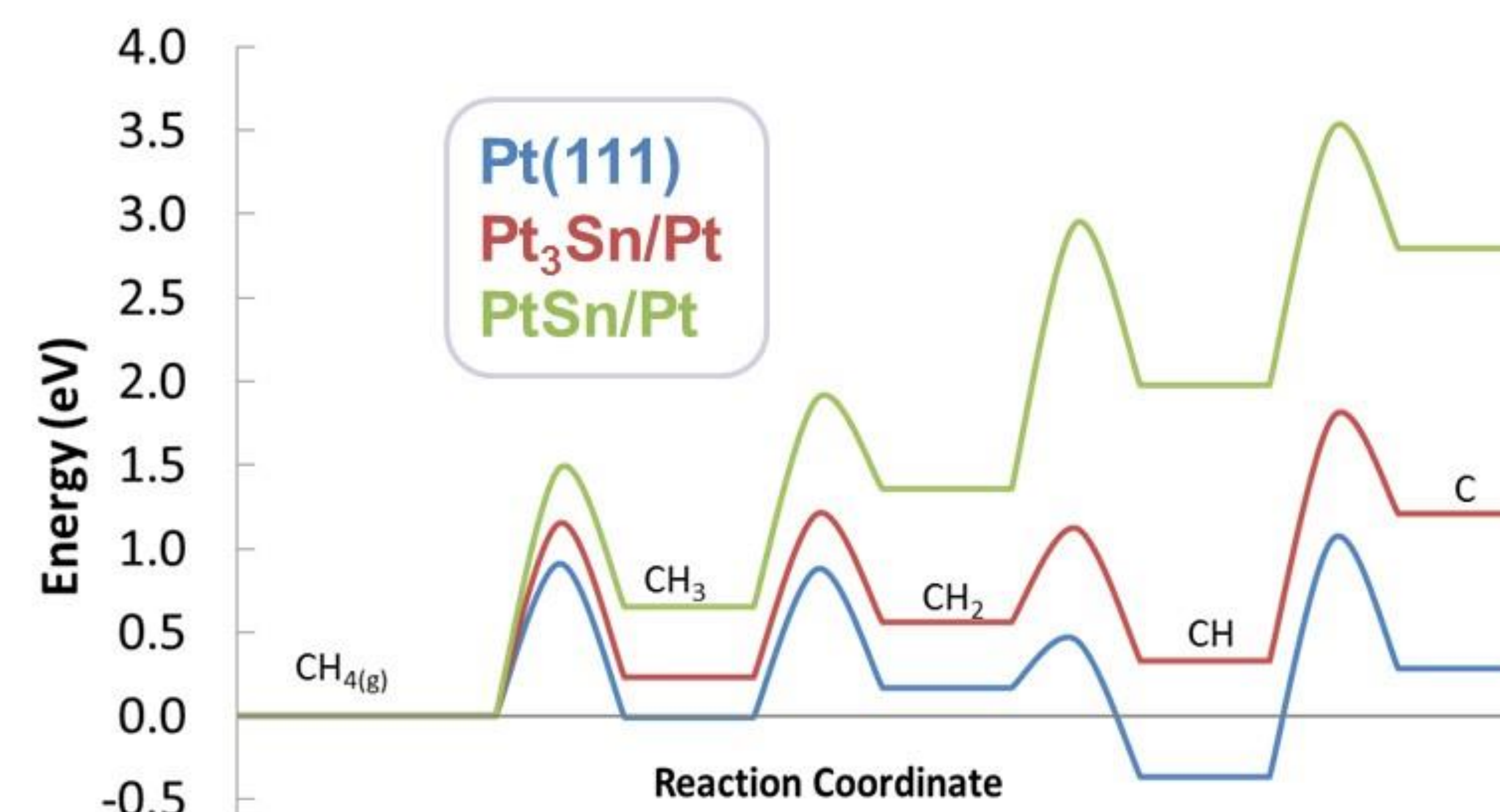


Reaction	Surface	E_a	ΔE	ΔE_a	$\Delta \Delta E$
$CH_3^* + * \rightarrow CH_2^* + H^*$	Pt(111)	0.88	0.35	0.00	0.00
	Pt ₃ Sn/Pt	0.98	0.45	0.10	0.10
	PtSn/Pt	1.25	0.95	0.37	0.60
$CH_2^* + * \rightarrow CH^* + H^*$	Pt(111)	0.27	-0.35	0.00	0.00
	Pt ₃ Sn/Pt	0.55	0.06	0.28	0.41
	PtSn/Pt	1.59	1.13	1.32	1.48
$CH^* + * \rightarrow C^* + H^*$	Pt(111)	1.42	0.86	0.00	0.00
	Pt ₃ Sn/Pt	1.46	1.08	0.04	0.22
	PtSn/Pt	1.54	0.72	0.12	-0.14

- All bonding involves Pt when possible
- Reaction pathway for Pt(111) & Pt₃Sn/Pt have identical reaction states
 - Differences in E_a and ΔE are primarily electronic effects
- High Sn loading on PtSn/Pt leads to some geometric changes

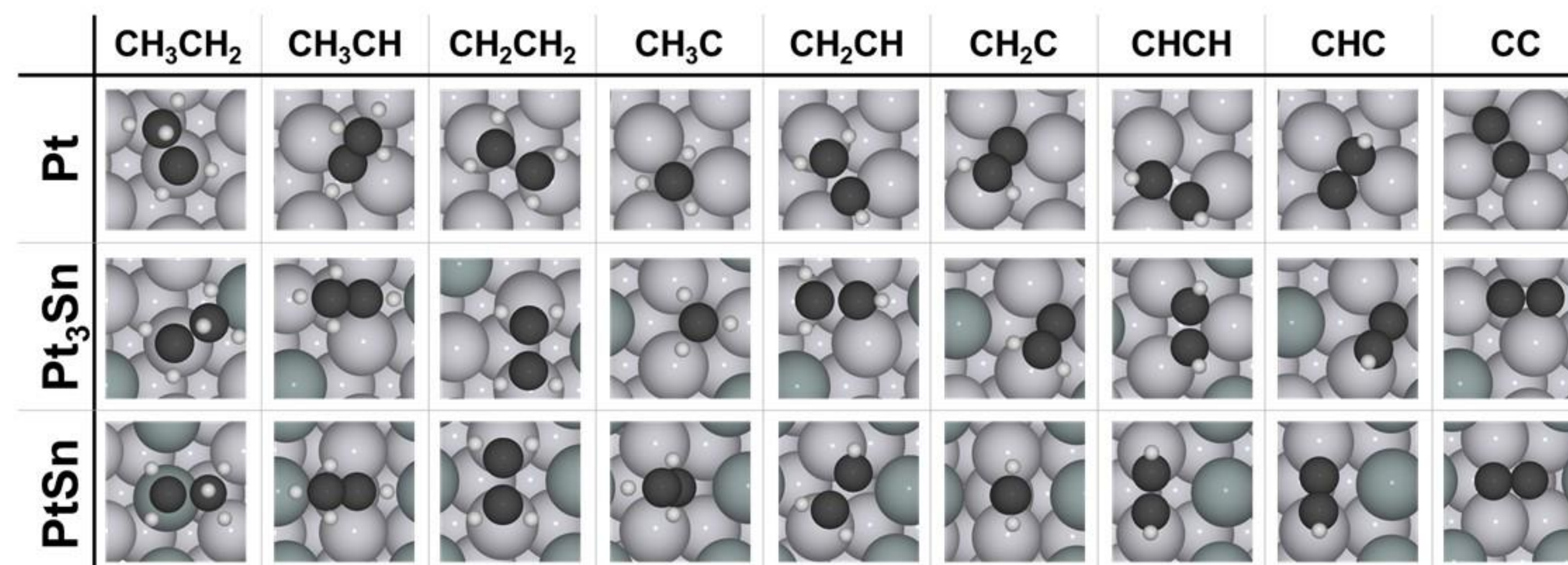
- Increasing Sn:
 - Weaker Binding
 - C-H bond cleavage is more endothermic
 - E_a is higher
 - Diffusion is harder¹
- Effect of alloy is greater on ΔE than E_a
- Geometric changes show larger effects than electronic

Single Carbon Potential Energy Surface



- Sn makes all C-H splitting steps more endothermic
- Barriers increase with increasing Sn coverage
 - Sn makes kinetics and thermodynamics harder
- Methylidyne (CH) is the global minimum on Pt
 - Local minimum on Pt₃Sn/Pt
- All steps are endothermic on PtSn/Pt
 - Atomic carbon formation becomes significantly harder, up to 2.5eV
- C-H Barriers in endothermic direction have similar barriers

Ethane Derivative Binding Geometries



- Binding modes typically avoid Sn atoms
- C-Sn bonds distort fcc structure
- Sn-top position not reactive
 - Only species forming CH₃ use Sn top position
- Carbon sp³ hybridization still preferred
 - σ -bonding more favorable than π -bonding modes
 - sp² preferred over Sn bonding