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Computational Progress of Designing Single Atom Alloy Catalysts for Methane Activation

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Abstract

Nonoxidative coupling of methane to value-added hydrocarbons remains a major challenge in catalysis due to inert C-H bonds in methane and rapid catalyst deactivation caused by coke contamination. Single atom alloys (SAAs), atomically dispersing isolated metal atoms into a host metal surface, have emerged as promising catalysts for activating light alkanes. Here, we present a review of recent progress on designing SAA catalysts for efficient and selective conversion of methane and other alkanes using computational modeling tools, including quantum mechanical simulations and machine learning models. First, we describe the various studies of applying first-principles simulations to discern reaction mechanisms, to understand the role of isolated dopant atoms in reducing C-H activation barriers, and to rationalize the synergy between dopant and host in improving selectivity towards desired products. Next, we present how the rapid development of machine learning models enables high-throughput screening of a large chemical space of SAA catalysts for methane transformation. We then extend the discussion from methane to the chemistry of activating other light alkanes, demonstrating the transferability of the synergy between dopant and host to activate multi-carbon hydrocarbons. Finally, we provide some perspectives on the future outlook for computational SAA catalyst design for methane activation. The goal of this review article is to present a computational perspective that systematically bridges first-principles mechanistic insights with data-driven workflows to enable the discovery of active, selective, and coke-resistant SAA catalysts for methane and light-alkane activation.

Keywords: Single Atom Alloy; Methane Activation; Nonoxidative Coupling of Methane; First-Principles Simulation; Machine Learning



1. Introduction

Methane, due to its substantial reserves in natural gas and shale formations, is an abundant carbon feedstock for chemical production.^{1, 2} However, its industrial valorization remains dominated by an indirect route, i.e., steam methane reforming to generate syngas followed by Fischer-Tropsch synthesis.³ Although being established and scalable, this route requires enormous energy consumption and suffers from rapid catalyst deactivation caused by coke formation, leading to low thermodynamic efficiency and massive CO₂ emissions.^{2, 4-6} Two challenges of efficiently converting methane into value-added multi-carbon hydrocarbons, such as ethylene,^{1, 7} are that: 1) the C-H bond in CH₄ is exceptionally strong with ~439 kJ/mol, demanding high temperatures over 700 °C,^{8, 9} and 2) partially dehydrogenated intermediates are strongly chemisorbed on catalyst surfaces, leading to catalyst deactivation.^{10, 11} Nonoxidative coupling of methane, bypassing syngas formation, is more environmentally and economically desirable.^{12, 13} However, it still faces the above two challenges.¹⁴⁻¹⁸ Thus, a catalyst that can simultaneously activate C-H bonds and enable C-C coupling to avoid full dehydrogenation is promising for efficient and selective conversion of methane to multi-carbon hydrocarbons.^{7, 19}

Single-atom alloys (SAAs), atomically dispersing active metal atoms into less active metal surfaces, have emerged as promising catalysts to overcome the above challenges in methane activation (Figure 1).²⁰⁻³⁵ The synergy between active dopants and host metal lowers the C-H activation barriers and simultaneously moderates binding strength of carbonaceous adsorbates to promote selective C-C coupling.^{19, 25} SAA catalysts such as Pt/Cu and Rh/Cu (i.e., one Pt atom and one Rh atom doped into Cu surface, respectively) have experimentally shown remarkable alkane dehydrogenation performance.^{28, 29} These SAA catalysts are able to operate at much lower temperatures (< 400 °C) than their counterpart host metals (> 900 °C) while achieving high selectivity towards desired products (> 90%) and enhanced resistance to coking.^{27-29, 36-40} However, mechanistic understanding of SAAs across compositions, facets, and operating conditions are necessary towards designing more efficient SAAs.



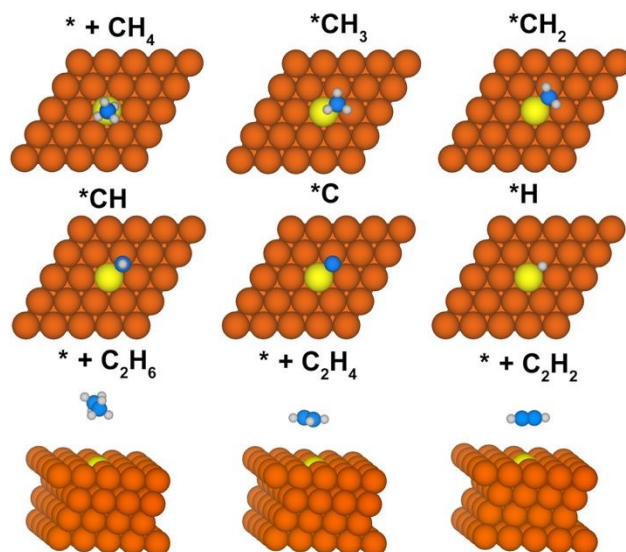


Figure 1. Representative structures of methane activation and C-C coupling mechanisms to C_2 products on SAAs. Atoms are colored as follows: orange for host metal, yellow for dopant metal, blue for carbon, and light gray for hydrogen.

Computational modeling plays a critical role in revealing reaction mechanisms of generating critical hydrocarbons,⁴¹⁻⁴³ providing atomic-level understanding of catalyst reactivity, and thus accelerating catalyst discovery.⁴⁴⁻⁴⁹ Density functional theory (DFT) calculations reveal important chemical insights through predictions of adsorption energies and reaction mechanisms on well-defined active sites in SAA catalysts.^{24, 28, 34, 35, 50-60} Combining free energy calculations with *ab initio* molecular dynamics (AIMD) simulations can capture temperature and entropic effects, ensuring thermodynamically consistent descriptions of reaction energies under experimentally relevant conditions.^{53, 61, 62} Microkinetic modeling further incorporates experimental operating conditions and then translates elementary-step kinetics into macroscopic observables, connecting computational predictions with experimental observations in SAA catalyst design.⁶²⁻⁶⁵ However, DFT simulations demand extensive computational resources for a large SAA chemical space and thus limit the scalability of DFT for SAA catalyst discovery.⁶⁶⁻⁶⁹ Consequently, substantial efforts have been devoted to reducing the computational cost by developing simple yet reliable descriptors (i.e., adsorption energies) and design principles (i.e., Sabatier principle) derived from DFT calculations.⁷⁰⁻⁷⁵ Building on the first-principles framework, machine learning (ML) provides a high-throughput screening strategy for accelerating SAA discovery.^{63, 64, 76-80} Trained on carefully constructed DFT datasets, ML models can achieve near DFT-level accuracy across broad compositional and structural spaces, enabling



efficient screening over various dopants, hosts, and facets, and provide interpretable insights into catalyst activity and selectivity.⁷⁷⁻⁸¹

This review focuses on computational progress of discovering SAA catalysts for direct methane activation with an extension to other alkanes activation, including ethane and propane. We first provide first-principles insights into SAAs for nonoxidative coupling of methane, including elucidating reaction mechanisms, developing effective descriptors, and performing microkinetic modeling. We then introduce ML models for SAA discovery, including dataset generation, model development, and results interpretation. We also extend the review to the activation of other alkanes, such as ethane and propane dehydrogenation, to understand the generalizability of SAAs in activating long-chain hydrocarbons. We close by summarizing key chemical insights and proposing strategies and principles for the future design of reactive, selective, and stable SAA catalysts for alkane activation.

2. First-Principles Studies on SAAs for Methane Activation

First-principles methods, particularly DFT, enable the prediction of reaction energetics and thus provide mechanistic insights into how isolated dopants reduce C-H activation barriers. These studies identify key catalytic descriptors underlying dopant-host synergy, including intermediate adsorption energies and transition-state geometries. In addition, first-principles calculations generate the datasets used to train the ML models discussed in the subsequent section on ML studies. Therefore, establishing a first-principles understanding of the electronic properties and reaction mechanisms governing methane activation is a critical prerequisite for implementing data-driven ML approaches.

Kokalj et al.⁵⁰ performed one of the earliest DFT studies with the Perdew-Burke-Ernzerhof (PBE)⁸² exchange-correlation (XC) functional on methane dehydrogenation over a Rh/Cu(111) SAA (the notation A/B denotes a single atom A dispersed in the surface layer of host B). They found that by dispersing a highly active Rh atom in the surface layer of a less reactive Cu(111) surface, the barrier for the first C-H bond breaking (i.e., $^*\text{CH}_4 \rightarrow ^*\text{CH}_3 + ^*\text{H}$, * denotes adsorbed species) can be largely reduced from 1.7 eV to 0.7 eV, which is almost identical to 0.69 eV on a pure Rh(111). Interestingly, the subsequent dehydrogenation step, i.e., $^*\text{CH}_3 \rightarrow ^*\text{CH}_2 + ^*\text{H}$, is kinetically more difficult than the first step due to the blockage of the active sites around $^*\text{CH}_3$, suggesting that Rh/Cu(111) SAA catalyst can effectively suppress



further dehydrogenation and thus mitigate coke formation. This work established a key foundation in SAA catalysis, in which the synergy between active dopants and less active hosts can decouple sequential dehydrogenation steps, enhancing both activity and selectivity. Zhang et al.⁵² further investigated the role of Rh dopants in enhancing the catalytic reactivity of Cu(111) surfaces for methane activation using DFT calculations with the Perdew-Wang 91 (PW91) XC functional⁸³. This work compared reaction barriers of methane dehydrogenation on a pure Cu(111), a single Rh atom adsorbed on Cu(111), and a Rh/Cu(111) SAA. An embedded Rh atom was found to substantially lower the barrier for the first C-H bond cleavage from 2.16 eV on pure Cu(111) to 0.87 eV on Rh/Cu(111), indicating the great potential of Rh as a dopant to facilitate methane dehydrogenation. The barriers for the second, third, and fourth dehydrogenation steps are similarly reduced, from 1.72 to 1.17 eV, from 1.30 to 0.97 eV, and from 2.30 to 1.50 eV, respectively. Interestingly, a single Rh adatom on Cu(111) exhibits comparable activity in lowering the first and second C-H activation barriers. However, the barrier for the third dehydrogenation step remains higher on the Rh adatom surface (1.30 eV) than on Rh/Cu(111) SAA (0.97 eV). For the fourth dehydrogenation step, the barrier is lower on the Rh adatom surface (1.09 eV) than on Rh/Cu(111) SAA (1.50 eV), indicating the uniqueness of SAA in suppressing coke formation. Reaction energies and activation barriers of each methane dehydrogenation step on various SAAs are summarized in Table 1, grouped by host metals, including Ag, Au, Cu, Ni, Pt, and Rh.

Table 1. Reaction energies (ΔE_{rxn}) and activation barriers (E_{a}) in eV of methane dehydrogenation steps on various SAA surfaces, along with the applied DFT XC functionals and references, reported in literature. Table 1 highlights three mechanistic trends emerging from reported DFT studies: 1) introducing an isolated dopant substantially lowers the barrier of the initial C-H activation compared with the pure host metal, thereby making methane activation kinetically accessible, 2) among the widely studied SAAs featuring Ni, Pd, Pt, Rh dopants on Ag, Au, Cu hosts, Rh-doped SAAs consistently exhibit the lowest barrier for the first C-H cleavage, and 3) when full dehydrogenation mechanisms are reported (e.g., for Cu- and Ni-host cases), the last step ($\text{*CH} \rightarrow \text{*C} + \text{*H}$) is rate-limiting, highlighting that high activity for the first dehydrogenation step does not necessarily imply facile deep dehydrogenation.

SAAs	$\text{CH}_4 \rightarrow \text{*CH}_3 + \text{*H}$		$\text{CH}_3 \rightarrow \text{*CH}_2 + \text{*H}$		$\text{CH}_2 \rightarrow \text{*CH} + \text{*H}$		$\text{CH} \rightarrow \text{*C} + \text{*H}$		XC functional	Ref.
	E_{a}	ΔE_{rxn}	E_{a}	ΔE_{rxn}	E_{a}	ΔE_{rxn}	E_{a}	ΔE_{rxn}		
	Ag Host									
Ni/Ag(111)	0.82	0.69	-	-	-	-	-	-	optB86b-vdW	24



Pd/Ag(111)	1.21	1.02	-	-	-	-	-	-	optB86b- vdW	24
Pt/Ag(111)	0.94	0.59	-	-	-	-	-	-	optB86b- vdW	24
Rh/Ag(111)	0.55	0.35	-	-	-	-	-	-	optB86b- vdW	24
Au Host										
Ni/Au(111)	0.94	0.94	-	-	-	-	-	-	optB86b- vdW	24
Pd/Au(111)	1.18	1.02	-	-	-	-	-	-	optB86b- vdW	24
Pt/Au(111)	0.85	0.56	-	-	-	-	-	-	optB86b- vdW	24
Rh/Au(111)	0.61	0.47	-	-	-	-	-	-	optB86b- vdW	24
Cu Host										
Pure Cu(111)	1.30	0.50	1.16	0.61	0.85	0.34	1.71	1.14	optB86b- vdW	29
Pure Cu(111)	2.16	0.85	1.72	0.86	1.30	0.64	2.30	1.42	PW91	52
Pure Cu(111)	1.77	1.07	1.62	1.12	1.13	0.88	2.06	1.82	PW91	54
Pure Cu(111)	1.32	-	1.24	-	0.87	-	2.03	-	PBE	56
Cr/Cu(111)	0.64	0.22	0.76	0.24	0.24	-0.11	1.26	0.76	PBE	35
Ir/Cu(111)	0.25	-0.01	0.59	0.32	0.42	-0.09	1.13	0.46	PBE	35
Ni/Cu(111)	0.82	0.56	-	-	-	-	-	-	optB86b- vdW	24
Ni/Cu(111)	0.77	0.43	0.75	0.50	0.54	0.35	1.33	0.84	PBE	35
Ni/Cu(111)	0.99	0.41	0.71	0.46	0.59	0.28	1.51	1.20	PW91	54
Pd/Cu(111)	1.19	0.80	-	-	-	-	-	-	optB86b- vdW	24
Pd/Cu(111)	1.27	0.67	1.26	0.91	1.07	0.71	1.92	1.42	PW91	54
Pd/Cu(111)	0.84	-	1.11	-	0.80	-	1.98	-	PBE	56
Pt/Cu(111)	0.92	0.53	-	-	-	-	-	-	optB86b- vdW	24
Pt/Cu(111)	0.86	0.30	0.96	0.62	0.75	0.31	1.49	0.90	optB86b- vdW	29
Pt/Cu(111)	1.11	0.40	1.11	0.73	1.07	0.65	1.86	1.39	PW91	54
Rh/Cu(111)	0.64	0.34	-	-	-	-	-	-	optB86b- vdW	24
Rh/Cu(111)	0.57	0.38	0.54	0.42	0.38	0.13	1.20	0.69	optB86b- vdW	29
Rh/Cu(111)	0.35	0.08	0.71	0.38	0.51	0.20	1.22	0.51	PBE	35
Rh/Cu(111)	0.70	0.36	0.84	0.59	-	-	-	-	PBE	50
Rh/Cu(111)	0.87	0.41	1.17	0.55	0.97	0.23	1.50	0.73	PW91	52
Rh/Cu(111)	0.83	0.39	0.76	0.41	0.45	0.01	1.48	0.97	PW91	54
W/Cu(100)	0.70	-0.25	0.97	0.04	0.98	-0.43	1.25	0.27	PW91	55
Ni Host										
Pure Ni(111)	0.92	0.02	-	-	-	-	1.28	0.46	PBE	51



Pure Ni(111)	0.90	-0.53	0.71	0.03	0.25	-0.50	1.22	0.36	PBE	60
Pure Ni(100)	0.83	0.16	-	-	-	-	0.52	-0.25	PBE	51
Pure Ni(211)	0.53	-0.32	-	-	-	-	0.51	-0.22	PBE	51
Al/Ni(111)	1.65	-0.35	0.70	0.33	0.90	-0.78	1.17	0.29	PBE	60
Cu/Ni(111)	1.49	-0.18	1.19	0.09	0.60	-0.33	1.82	-0.12	PBE	60
Fe/Ni(111)	1.02	-0.36	0.94	-0.01	0.46	-0.33	1.26	0.49	PBE	60
Pd/Ni(111)	1.06	0.38	-	-	-	-	1.28	0.59	PBE	51
Pd/Ni(111)	1.08	-0.13	0.91	0.10	0.69	-0.54	1.59	0.47	PBE	60
Pd/Ni(100)	0.94	0.27	-	-	-	-	0.74	-0.03	PBE	51
Pd/Ni(211)	0.62	0.06	-	-	-	-	0.66	-0.09	PBE	51
Pt/Ni(111)	0.89	-0.07	0.63	-0.21	0.82	-0.40	1.43	0.52	PBE	60
Zn/Ni(111)	0.95	0.02	1.86	0.07	0.57	-0.89	1.16	0.28	PBE	60
Pt & Rh hosts										
Pure Pt(111)	0.51	-0.27	0.58	-0.06	0.10	-0.71	1.16	0.41	optB86b-vdW	29
Pure Rh(111)	0.46	-0.30	0.31	-0.28	0.04	-0.56	1.01	0.32	optB86b-vdW	29
Pure Rh(111)	0.69	0.22	0.42	-0.10	-	-	-	-	PBE	50

A screening work was later conducted using DFT with the optB86b-vdW XC functional⁸⁴⁻⁸⁷ by Darby et al.²⁴ to examine methane adsorption and the first C-H bond cleavage of methane across 12 SAA catalysts, comprising active dopants of Ni, Pd, Pt, and Rh embedded in less reactive host metals of Cu(111), Ag(111), and Au(111). They showed that the dopant sites are the dominant active sites, i.e., CH₄ activation occurring at the dopant top site where the transition state structure is stabilized by the active dopant. Subsequently, the dissociated *H migrates to a dopant-host interfacial hollow site while *CH₃ remains on the dopant top site. The reactive dopants result in surmountable barriers of the first C-H bond breaking step, including 0.82 eV for both Ni/Ag(111) and Ni/Cu(111); 0.94, 0.85, and 0.92 eV for Pt/Ag(111), Pt/Au(111), Pt/Cu(111); and particularly low barriers of 0.55, 0.61, and 0.64 eV for Rh/Ag(111), Rh/Au(111), Rh/Cu(111). The isolated dopants remarkably lower the reaction barriers of C-H bond cleavage compared to the pure metal hosts (2.11, 1.78, and 1.48 eV for Ag, Au, and Cu), achieving barriers close to their corresponding bulk materials (Ni(111): 0.75 eV; Pd(111): 0.68 eV; Pt(111): 0.58 eV; Rh(111): 0.56 eV). In addition, Figure 2 demonstrates that the Brønsted-Evans-Polanyi (BEP) relationship remains valid across the 12 SAAs but shifts towards a lower reaction barrier compared to pure metals due to the dopant-host synergy. In general, SAAs tune



adsorbate binding energy to achieve intermediate strengths between those on host metals and dopant metals, to both enhance reactivity and reduce coke formation.

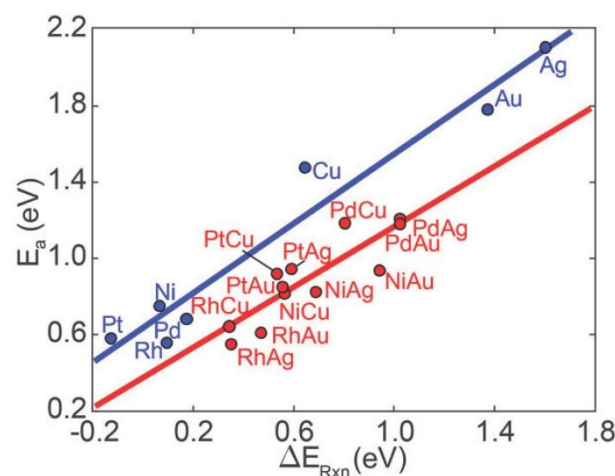


Figure 2. BEP relationship for the first C-H bond cleavage in methane on pure metal surfaces (blue) and SAA surfaces (red). The activation energy (E_a) is plotted against the reaction energy (ΔE_{Rxn}) with linear fitting lines shown for each surface type. Reproduced from Ref.²⁴ with permission from American Chemical Society, copyright 2018.

In addition to the initial methane dehydrogenation step, Jiang et al.⁵⁴ employed DFT with the PW91 XC functional to study the complete methane dehydrogenation pathway on pure Cu(111) and Cu(111)-based SAAs with Pd, Pt, Rh, and Ni single dopants (Table 1). All studied SAAs exhibit enhanced activity compared to pure Cu(111) with significantly decreased reaction barriers for all C-H bond cleavages of CH_4 . In addition, they found that the activity trend follows $\text{Rh} > \text{Ni} > \text{Pt} > \text{Pd}$ in terms of both kinetic and thermodynamic favorability, consistent with the findings of Darby et al.²⁴ Particularly, Rh/Cu(111) SAA exhibits the lowest reaction energies and activation barriers for all dehydrogenation steps, making it the optimal SAA catalyst for methane activation. Furthermore, the last dehydrogenation step of $^*\text{CH} \rightarrow ^*\text{C} + ^*\text{H}$ was identified as the universal rate-limiting step across all studied SAAs, consistent with previous studies.⁵² This work shows that all four active dopants can improve reactivity of Cu surface for methane activation with Rh/Cu(111) SAA as the most promising one.

Hannagan et al.²⁹ studied the same dopants of Ni, Pd, Pt, and Rh, but extended the host metals from Cu(111) to Ag(111) and Au(111) for methane activation using DFT with optB86b-vdW XC functional. They also found that the Rh-doped SAAs exhibit the lowest C-H activation barriers, consistent with previous studies showing the great potential of Rh dopant in activating



methane.^{24, 52, 54} Among different metal hosts, Rh/Cu(111) exhibits both lower C-H activation barriers and higher thermodynamic stability (Figure 3A). Electronic structure analysis reveals that methane adsorbs closer to the Rh dopant site on Rh/Cu(111) than to Cu site on pure Cu(111) and exhibits stronger charge redistribution from C-H bond to H...Rh internuclear region than on pure Cu(111), indicating activation of methane upon adsorption on Rh/Cu(111) SAA (Figure 3B). Reaction energy profiles indicate that further dehydrogenation steps leading to coke formation occur more easily on pure Pt(111) than on pure Cu(111) and Rh/Cu(111) SAA surfaces, whereas the subsequent dehydrogenation steps are unfavored on Rh/Cu(111) due to the predicted large reaction energies (Figure 3C). Akça⁵⁶ performed a detailed study of methane dehydrogenation on Pd/Cu(111) SAA using DFT with PBE XC functional, confirming that incorporation of Pd dopants reduces the barriers of the initial C-H bond cleavage by 0.48 eV compared to a pure Cu(111) surface, whereas showing negligible effects on the second and third steps.



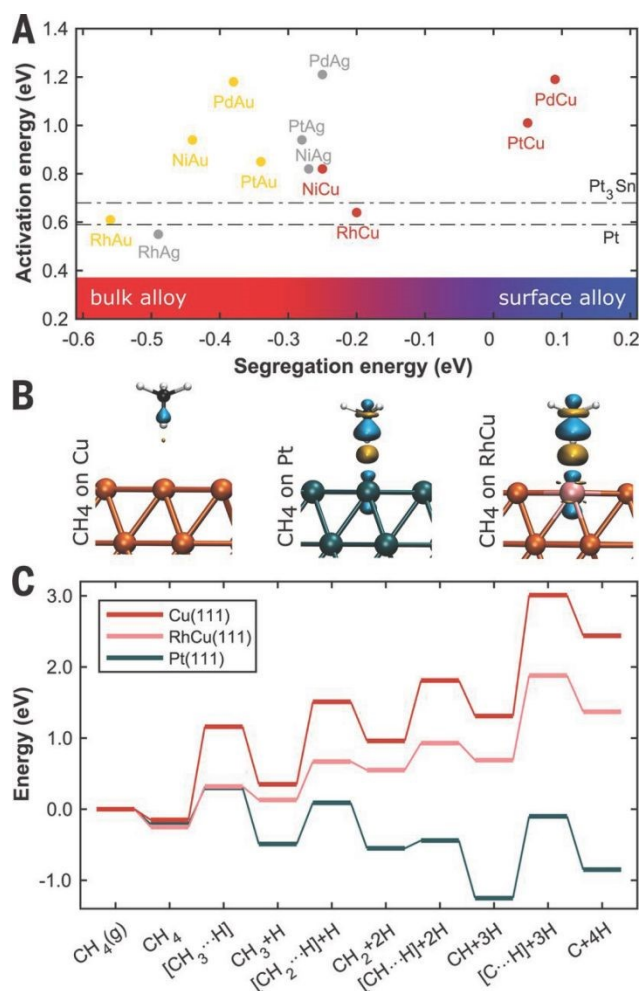


Figure 3. (A) Relationship between the activation barriers of the first C-H bond cleavage on various SAAs and the SAA segregation energies. Activation barriers on Pt(111) and Pt₃Sn are shown as dotted dash lines. (B) Charge density difference of CH₄ adsorbed on Cu(111), Pt(111), and Rh/Cu(111) SAA surfaces. Cu, Pt, and Rh atoms are colored as orange, teal, and pink, respectively. Cyan and yellow contours indicate regions of electron depletion and accumulation with isosurface value of $\pm 0.01 \text{ e}/\text{\AA}^3$. (C) Energy profiles of full methane dehydrogenation steps on pure Cu(111) (red), Rh/Cu(111) (pink), and pure Pt(111) (green) surfaces. Reproduced from Ref.²⁹ with permission from AAAS, copyright 2021.

Marcinkowski et al.²⁸ combined DFT with optB86b-vdW XC functional, surface science experiments, and microkinetic modeling to explore the catalytic reactivity of Pt/Cu(111) SAA for C-H activation and demonstrated that Pt/Cu SAA can efficiently activate C-H bonds while resisting coke formation. Isolated Pt atoms dispersed on a Cu(111) surface serve as highly active sites that lower the first C-H bond activation barrier from 1.48 eV on a pure Cu(111) surface to 0.92 eV. In general, reaction barriers for the full methane dehydrogenation steps on Pt/Cu(111) SAA are lower than those on a pure Cu(111), but higher than those on a pure Pt(111), enabling



methane dehydrogenation at lower temperatures than Cu(111) and simultaneously suppressing coke formation (Figure 4). Experimentally, Pt/Cu SAA is stable and active over a long operation time, while the monometallic Pt surface rapidly deactivates due to coke deposition. This work highlights that the SAA catalyst outperforms its pure metal components. Afterwards, Gerrits et al.⁵³ combined DFT with AIMD to investigate initial C-H bond activation of CHD₃ on Cu surfaces and Cu-based SAAs. Their findings are consistent with previous work that C-H activation barrier is dramatically reduced on Pt/Cu(111) and the C-H activation only occurs near the Pt top site.²⁸

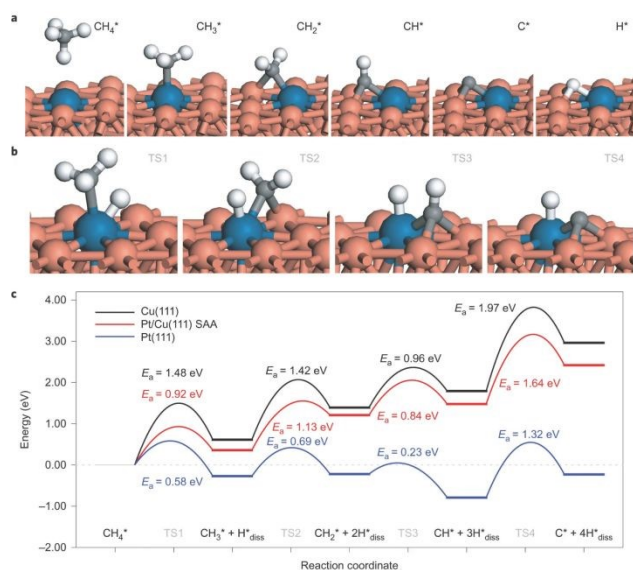


Figure 4. Methane dehydrogenation on pure Cu(111), Pt/Cu(111) SAA, and pure Pt(111) predicted by DFT. (a) Optimized geometries of the most stable methane dehydrogenation intermediates on Pt/Cu(111). (b) Transition state structures of successive C-H bond cleavages of methane dehydrogenation on Pt/Cu(111). (c) Energy profiles of full methane dehydrogenation on Cu(111) (black), Pt/Cu(111) SAA (red), and Pt(111) (blue). Reproduced from Ref.²⁸ with permission from Springer Nature, copyright 2018.

Zhao et al.⁵¹ extended the SAA studies from Cu to Ni metal host and employed DFT with the PBE⁸² XC functional to study the thermodynamic stability of Pd/Ni SAAs and how Pd doping influences methane dehydrogenation on Ni(111), Ni(100), and Ni(211) facets. They found that SAA with isolated Pd atoms embedded on the Ni surface layer has the most negative formation energy compared with Pd atoms immersed in the Ni bulk or adsorbed on the Ni surface, indicating formation of Pd/Ni SAAs. Interestingly, they predicted that although Pd dopants reduce binding strength of most intermediates, including *CH₃, *CH, *C, *H, they



increase activation barriers of both CH₄ and *CH dehydrogenation. This is divergent from Pd/Cu SAAs, likely due to the higher reactivity of Ni than Cu for methane activation.^{29, 54, 56} Among the Pd/Ni SAAs, CH₄ dehydrogenation is most favored on the stepped Pd/Ni(211) surface, followed by Pd/Ni(100) surface and then the close-packed Pd/Ni(111) surface (Table 1). In a different study by Dong et al.⁶⁰ focusing on Ni(111)-based SAAs with dopants spanning Cu, Fe, Pt, Pd, Zn and Al, they found that Al and Zn dopants can reduce the barrier of the final *CH → *C + *H step, whereas Pt dopant lowers the barriers of CH₄ → *CH₃ + *H and *CH₃ → *CH₂ + *H. Additionally, *C adsorbates tend to aggregate into forming graphitic layers, destabilizing surface intermediates and increasing activation barriers for all dehydrogenation steps. This explains the mechanisms of coke formation and how it suppresses further methane activation and deactivates catalyst surfaces.

Other recent DFT studies explored additional SAA dopants. For example, Khettal et al.⁵⁵ focused on the performance of W/Cu SAAs and found that W/Cu(100) exhibits surmountable reaction energies and activation barriers for CH₄ dehydrogenation, indicating that W may serve as an effective dopant to enhance methane activation on Cu surfaces. Ren et al.⁵⁷ used DFT with the PBE XC functional to examine methane activation on SAAs with Ir atoms atomically dispersed on several metal hosts, including Cu, Ag, Pd, Pt, Ni, and Rh with three exposed facets, i.e., (100), (110), and (111). Incorporation of Ir dopants into host metal surfaces effectively reduces reaction barriers of the first C-H bond cleavage step by approximately 0.3 to 0.4 eV compared with the corresponding pure metal host surfaces (Figure 5). Surprisingly, Ir dopants not only activate less reactive host metals, such as Cu and Ag, but also improve the activity of more reactive metals, including Pd, Pt, and Ni, revealed from their lower C-H activation barriers. The enhanced reactivity originates from the *d*-states of the Ir dopant, which promote electron transfer between surface and the C-H bond, thus stabilizing transition states and lowering the activation energies. Among all examined SAAs, Ir/Pt(110) has the highest catalytic activity with an activation barrier that is close to 0 eV, highlighting that SAAs with Ir dopants are promising catalysts for low-temperature methane activation. However, this study only focused on the first C-H bond breaking, overlooking further dehydrogenation steps that might lead to coke formation.²⁸



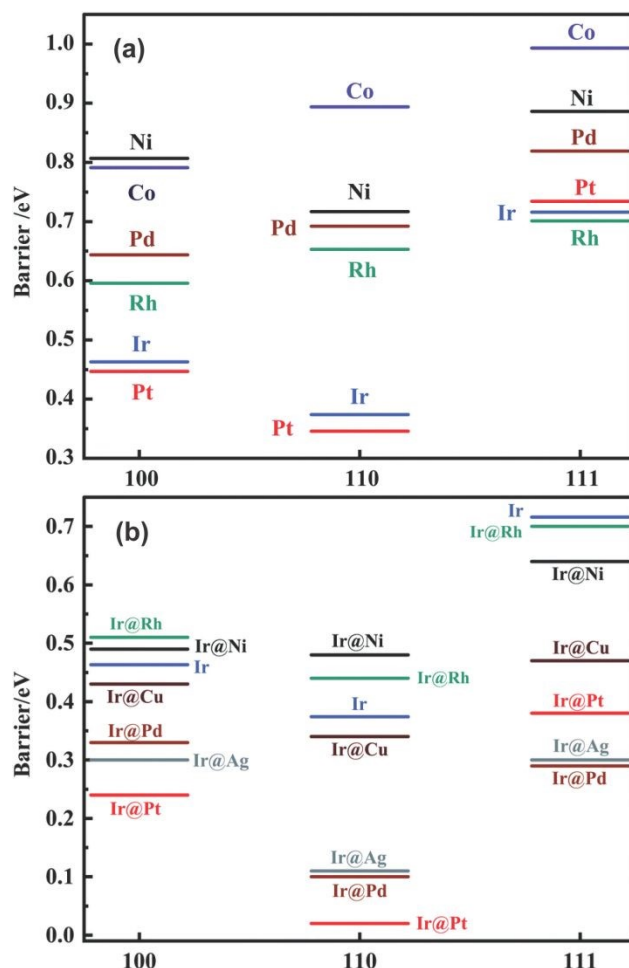


Figure 5. Activation barriers of first C-H bond breaking of methane on (a) pure metal surfaces and (b) SAA surfaces with Ir dopants across (100), (110), and (111) facets. Reproduced from Ref.⁵⁷ with permission from Royal Society of Chemistry, copyright 2021.

Zhou et al.⁵⁹ explored 12 SAAs for methane activation using DFT with PBE XC functional, including Ir, Ni, Pt and Rh dopants on Ag(111), Au(111), and Cu(111) metal hosts. Similarly, their results showed that SAAs with Ir dopants exhibit the highest activity for the first C-H bond cleavage compared with other dopants, arising from the strong interaction between the cleaved C-H bond and *d*-orbitals of Ir dopants, consistent with the above work.⁵⁷ Another work by Zhou et al.⁵⁸ screened a relatively large SAA chemical space of 12 metal dopants on 4 metal hosts, including Cu(111), Cu(100), Ag(111), and Ag(100) for the first C-H activation of methane using DFT with PBE XC functional. They found that even though the reaction energies and activation barriers generally follow the BEP relationship, relatively large mean absolute errors (MAE) of around 0.2 eV are observed (Figure 6). Instead, they proposed a new descriptor that



incorporates adsorption energies of $^*\text{CH}_3$ and $^*\text{H}$ intermediates to correlate with the C-H activation barriers across all studied SAAs (Figure 7), enabling accurate prediction of methane activation barriers on unexplored SAA surfaces.

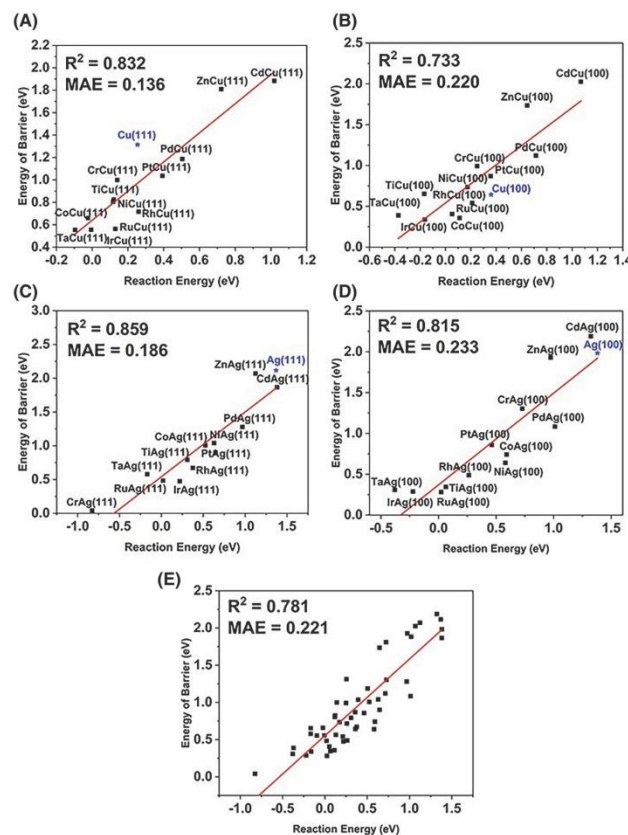


Figure 6. BEP relationship of the first C-H bond activation of methane on SAAs with: (A) Cu(111), (B) Cu(100), (C) Ag(111), (D) Ag(100), and (E) all metal hosts. Reproduced from Ref.⁵⁸ with permission from John Wiley and Sons, copyright 2023.



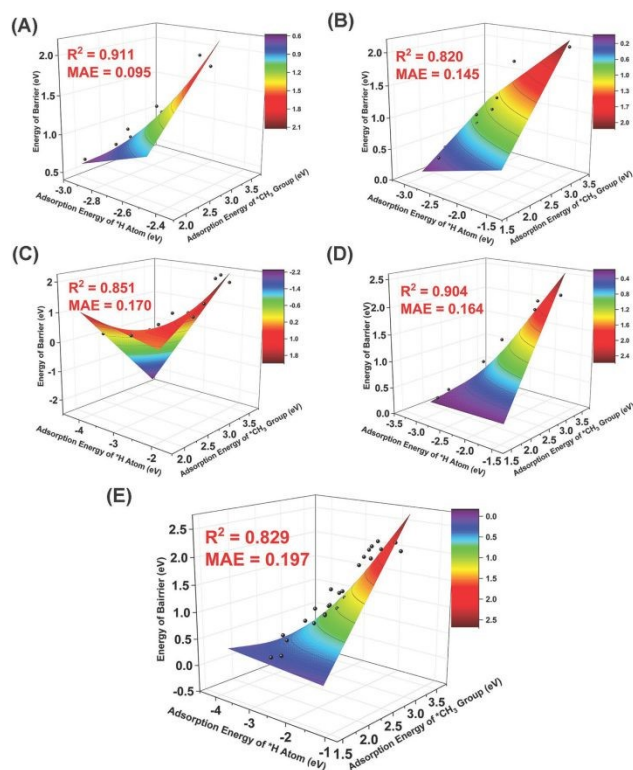


Figure 7. Relationship between a binary descriptor incorporating adsorption energies of *CH_3 and *H and reaction barriers of the first C-H activation of methane on SAAs with (A) Cu(111), (B) Cu(100), (C) Ag(111), (D) Ag(100), and (E) all metal hosts. Reproduced from Ref.⁵⁸ with permission from John Wiley and Sons, copyright 2023.

Beyond methane dehydrogenation, nonoxidative coupling of methane towards generating multi-carbon hydrocarbons represents a more industrially relevant and economic beneficial reaction.^{34, 35} Kothakonda et al.³⁴ performed a systematic screening of 27 Cu(111)-based SAAs with all possible 3d-5d transition metals for nonoxidative coupling of methane to C_2 products, including ethane and ethylene using DFT with PBE XC functional. They started by calculating aggregation and segregation energies of all dopant-host combinations to assess thermodynamic stabilities of SAAs and identified 16 stable SAAs for subsequent reactivity studies, including full dehydrogenation steps and possible C-C coupling steps to ethane and ethylene (Figure 8). Among them, further selectivity analyses indicated that Ni/Cu(111), Rh/Cu(111), and Cr/Cu(111) SAAs exhibit both high activity and selectivity towards C_2 products based on thermodynamic favorability. To provide a more complete picture, they further performed kinetic calculations of nonoxidative coupling of methane to both ethane and ethylene on these three SAA candidates and concluded that Ni/Cu(111) is a highly active and selective SAA for direct methane conversion to ethylene (Figure 8).



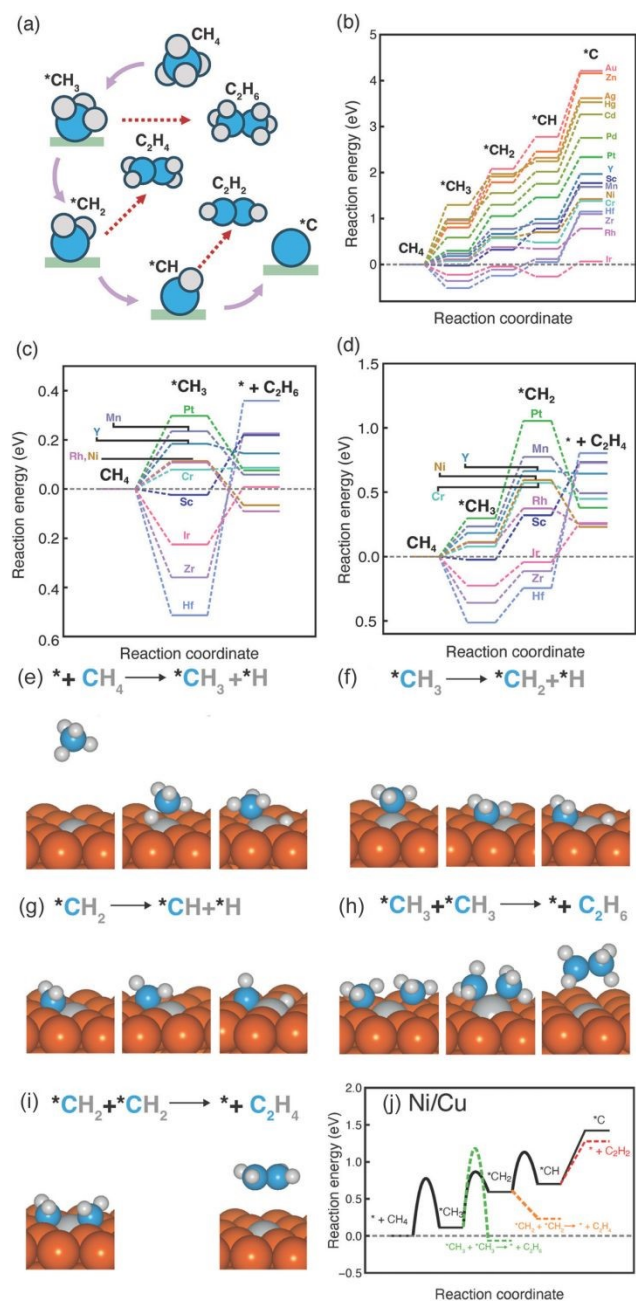


Figure 8. (a) Schematic of methane dehydrogenation to *C and C-C coupling steps forming ethane, ethylene, and acetylene. Atoms are colored as blue for carbon and gray for hydrogen. (b) Energy landscapes for full methane dehydrogenation to *C on 16 stable SAAs. Energy landscapes for direct methane conversion to (c) ethane and (d) ethylene on 10 stable SAAs with reaction energies of first dehydrogenation step below 0.5 eV. SAAs are labeled using the corresponding dopant element. Structures of initial, transition, and final states for (e-g) methane dehydrogenation and (h, i) C-C coupling to form C_2 products on Ni/Cu SAA. Energy landscapes for the full methane dehydrogenation to *C and C-C coupling to form C_2 products on (j) Ni/Cu



SAA. Reproduced from Ref.³⁴ with permission from American Chemical Society, copyright 2025.

Extending the work of Kothakonda et al.,³⁴ Zhou et al.³⁵ systematically computed reaction barriers of all steps of nonoxidative coupling of methane, including full dehydrogenation and two C-C coupling steps to ethane and ethylene, on ten Cu(111)-based SAAs, including Sc, Cr, Mn, Ni, Y, Zr, Rh, Hf, Ir, and Pt dopants, which show reaction energies of less than 0.5 eV for the first C-H bond activation. A strong correlation between SAA activity and selectivity toward ethylene formation was observed, indicating that the synergy between dopant and host can simultaneously reduce C-H activation barriers and promote selective C-C coupling (Figure 9). Interestingly, ethylene formation is kinetically favored over ethane formation across all studied SAAs (Figure 9). In addition, $^*\text{C}_2\text{H}_4$ adsorption energy was identified as an effective descriptor that correlates with SAA activity for direct methane conversion to ethylene (Figure 9). Among all candidates, Ir/Cu(111) SAA emerges as the most kinetically favorable catalyst for methane to ethylene conversion.



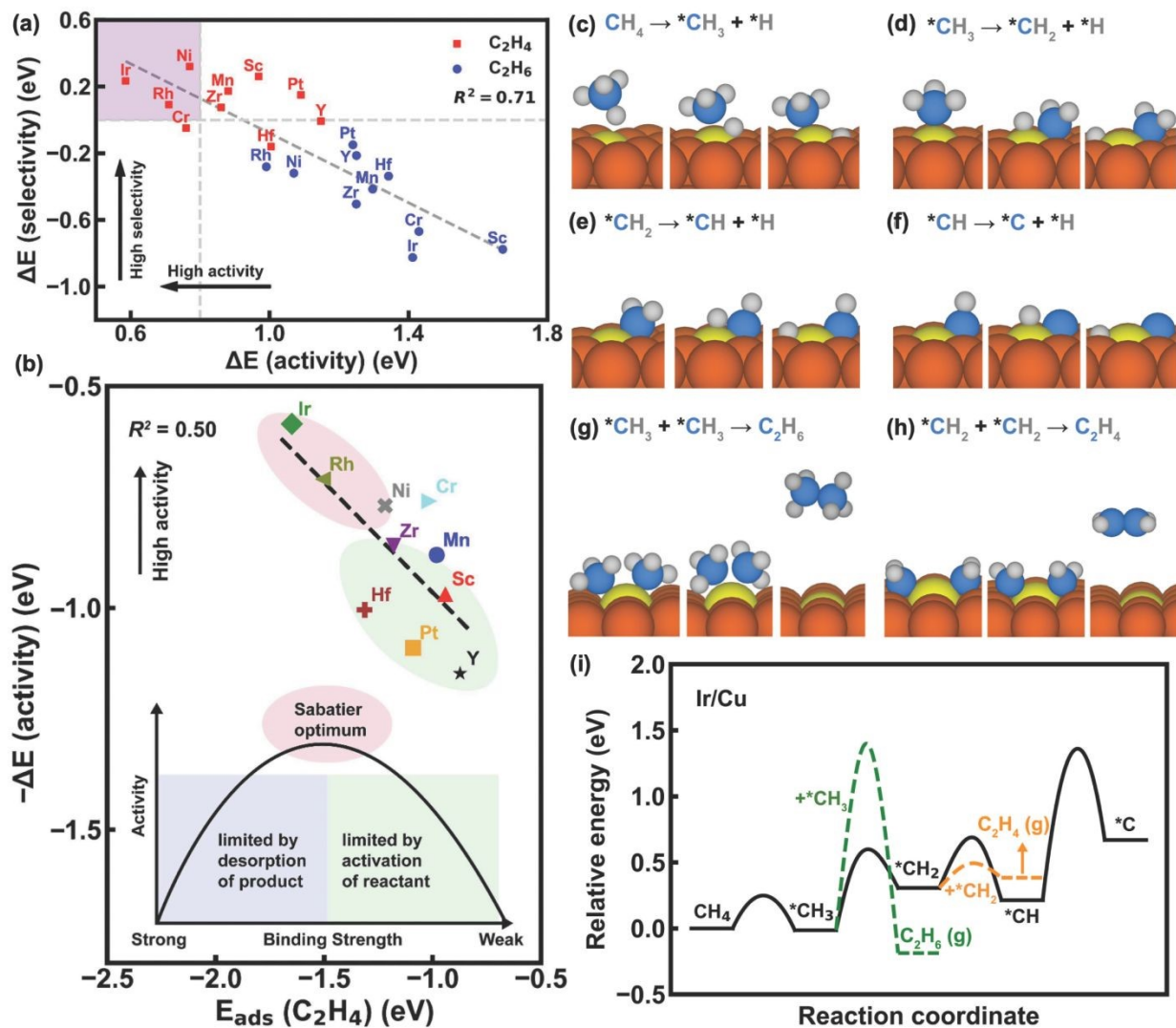


Figure 9. (a) Correlation between activity and selectivity of ten Cu-based SAA catalysts for direct methane conversion to ethane (blue circles) and ethylene (red squares). The dashed gray line shows the linear fit with R^2 inset. The vertical and horizontal gray dashed lines indicate an activity of 0.8 eV and a selectivity of 0.0 eV, respectively. The upper-left purple region indicates SAAs with both high activity and high selectivity. (b) Correlation between the negative reaction barrier of the rate-limiting step and the ethylene adsorption energy for ten SAAs. The dashed black line denotes the linear fit with R^2 inset. The inset schematic illustrates the Sabatier principle with the blue region representing desorption-limited reactivity and the green region representing activation-limited reactivity. Structures of initial, transition, and final states for (c-f) methane dehydrogenation steps and (g-h) C-C coupling steps to form C_2 products on Ir/Cu SAA. (i) Energy profile of methane dehydrogenation to $*C$ (black solid line), $*CH_3$ coupling to ethane (green dashed line), and $*CH_2$ coupling to ethylene (orange dashed line) on Ir/Cu SAA. Reproduced from Ref.³⁵ with permission from Elsevier, copyright 2025.



The wide range of activation barriers reported for a same SAA in Table 1 underscores the sensitivity of predicted methane activation energetics to the choice of DFT XC functionals. Early studies primarily employed standard generalized gradient approximation (GGA) functionals such as PBE⁸² and PW91,⁸³ which are generally suitable for describing metallic bonding but do not explicitly account for long-range dispersion interactions. This limitation can be important because methane adsorption is weak, and both the physisorbed initial state and the stretched C-H transition state may be stabilized when van der Waals (vdW) interactions are included. Dispersion-inclusive functionals, such as optB86b-vdW,⁸⁴⁻⁸⁷ can capture vdW interactions more accurately. However, they may overestimate adsorption energies for strongly chemisorbed intermediates, and thus often yield activation barriers that differ from those obtained with standard GGAs.^{88, 89} For example, for the Rh/Cu(111) SAA, the reported barrier for the first C-H cleavage ranges from 0.35 eV (PBE) to 0.87 eV (PW91), while an optB86b-vdW study reports an intermediate value of 0.57 eV for the same step. Similar variations are observed for the pure host metal that Cu(111) shows a first-step barrier of 2.16 eV in a PW91 study, compared with 1.30 eV obtained using optB86b-vdW. Importantly, despite these quantitative variations in activation barriers, the qualitative design trends for SAAs remain consistent across different functionals. Reactive dopants such as Rh and Ni substantially lower the first C-H activation barrier relative to the host metal regardless of functional choices, highlighting the robustness of DFT as a tool for studying SAA reactivity.

3. Machine Learning Studies on SAAs for Methane Activation

Over the past decade, ML has attracted great attention among the computational catalysis community for its capability in accelerating catalyst design through high-throughput screening.⁹⁰⁻¹⁰² ML serves as a fast and accurate alternative to first-principles modeling by learning structure-composition-property relationships from DFT-constructed datasets, and then infer physical correlations and predict catalytic behavior across vast chemical spaces, thus providing a scalable route to explore large compositional and structural domains.¹⁰³⁻¹¹⁰ However, it is challenging to accurately identify convoluted relationships between bulk/surface structures and catalytic performances, emphasizing the need for interpretable descriptors that govern activity and selectivity. This section summarizes recent ML-based efforts of discovering efficient catalysts for methane activation and unearthing key descriptors and design principles.



Toyao et al.⁷⁶ developed regression models to predict DFT-computed adsorption energies of methane dehydrogenation intermediates, $^*\text{CH}_x$ species ($x = 3, 2, 1, 0$) and $^*\text{H}$, on Cu(111)-based SAAs using 12 descriptors of the dopant physical properties.¹¹¹⁻¹¹⁴ DFT datasets contain 46 data points, i.e., 46 SAA surfaces, for each adsorbate. They systematically compared four regression models and found that extra tree regression (ETR) model shows the best performance in predicting the adsorption energies with the average root mean squared errors (RMSEs) below 0.3 eV. Feature importance analysis revealed that group in the periodic table, surface energies, and melting points of the dopant elements are the most important descriptors to predict the adsorption energies. Other work shows that group in the periodic table and surface energies are common descriptors for catalytic performances.^{115, 116} This ML model only requires small DFT datasets and negligible computational cost, and thus could be used to rapidly screen a large chemical space of SAA catalysts for methane activation. Later, Saxena et al.⁶³ employed a similar framework and selected the gradient boosting regression (GBR) model to predict atomic $^*\text{C}$ and $^*\text{O}$ binding energies on Cu-based SAAs using the same set of descriptors,^{113, 114, 117} achieving accuracies of RMSE below 0.4 eV. Similarly, feature importance analysis identifies surface energies and group in periodic table of dopants as dominant descriptors, consistent with the above work by Toyao et al.⁷⁶

Han et al.⁷⁸ integrated first-principles calculations with the compressed-sensing data-analytics method, namely the sure independence screening and sparsifying operator (SISSO) model, to identify the best low-dimensional descriptors that guide SAA catalyst design for industrially relevant reactions. They aimed at predicting H binding energies (BE_H), H_2 dissociation energy barriers (E_b), dopant segregation energies (SE), and dopant segregation energies in the presence of adsorbed hydrogen (SE_H). DFT datasets contain more than three hundred SAAs calculated with revised Perdew-Burke-Ernzerhof (RPBE) functional.¹¹⁸ Standard correlations in computational catalyst design based on d -band center theory^{67, 119} and BEP relationship unfortunately fail for H adsorption on SAAs, emphasizing the need for new descriptors and SAA design principles. Instead, SISSO model shows good predictive accuracy and was used to perform high-throughput screening of 5,000 SAA catalysts for hydrogen dissociation reactions through predicting BE_H , E_b , and SE_H . An activity descriptor incorporating E_b and the free energy of H adsorption (ΔG) as $\sqrt{\Delta G^2 + E_\text{b}^2}$ was developed to build a correlation between SAA reactivity and stability, and then over 200 SAA candidates with high activity and



stability were identified (Figure 10). Overall, this study provides a robust, generalizable, and accelerated approach for evaluating SAA stability and activity.

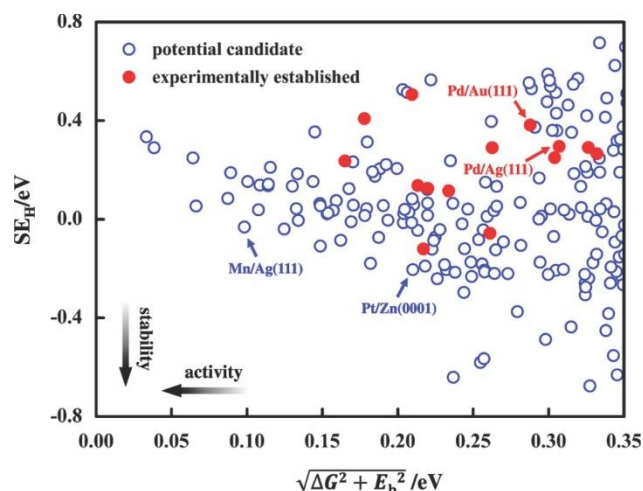


Figure 10. Correlation between stability and activity of experimentally established SAAs (red filled circles) and SISSO-predicted SAAs (blue empty circles). The y-axis represents the stability descriptor, SE_H , while x-axis represents the activity descriptor, $\sqrt{\Delta G^2 + E_b^2}$. Reproduced from Ref.⁷⁸ with permission from Springer Nature, copyright 2021.

Sun et al.⁷⁹ developed a ML framework to discover SAA catalysts for the chemistry of methane activation through learning DFT-computed reaction barriers of C-H cleavage and screening a large chemical space of 10,950 SAA surfaces. They first constructed 623 DFT energy barrier data points of the first and last steps of methane dehydrogenation to train an ML regression model. Then the ML regression model was used to screen 10,950 SAA surfaces. Feature importance analysis suggests that a descriptor related to surface energy is the dominant one (Figure 11), consistent with the above findings.^{63, 76} This ML workflow identified two highly active and selective SAA catalysts for methane cracking, Ir/Ni(111) and Re/Ni(111). Subsequent experimental work confirms high H_2 yield rates and reasonable methane conversion rates for both ML-predicted SAAs. This study demonstrates the efficiency and robustness of data-driven ML model in accelerating SAA catalyst design and discovering experimentally viable catalysts for methane activation. Detailed ML workflow is covered in another work (Figure 11d).⁸⁰



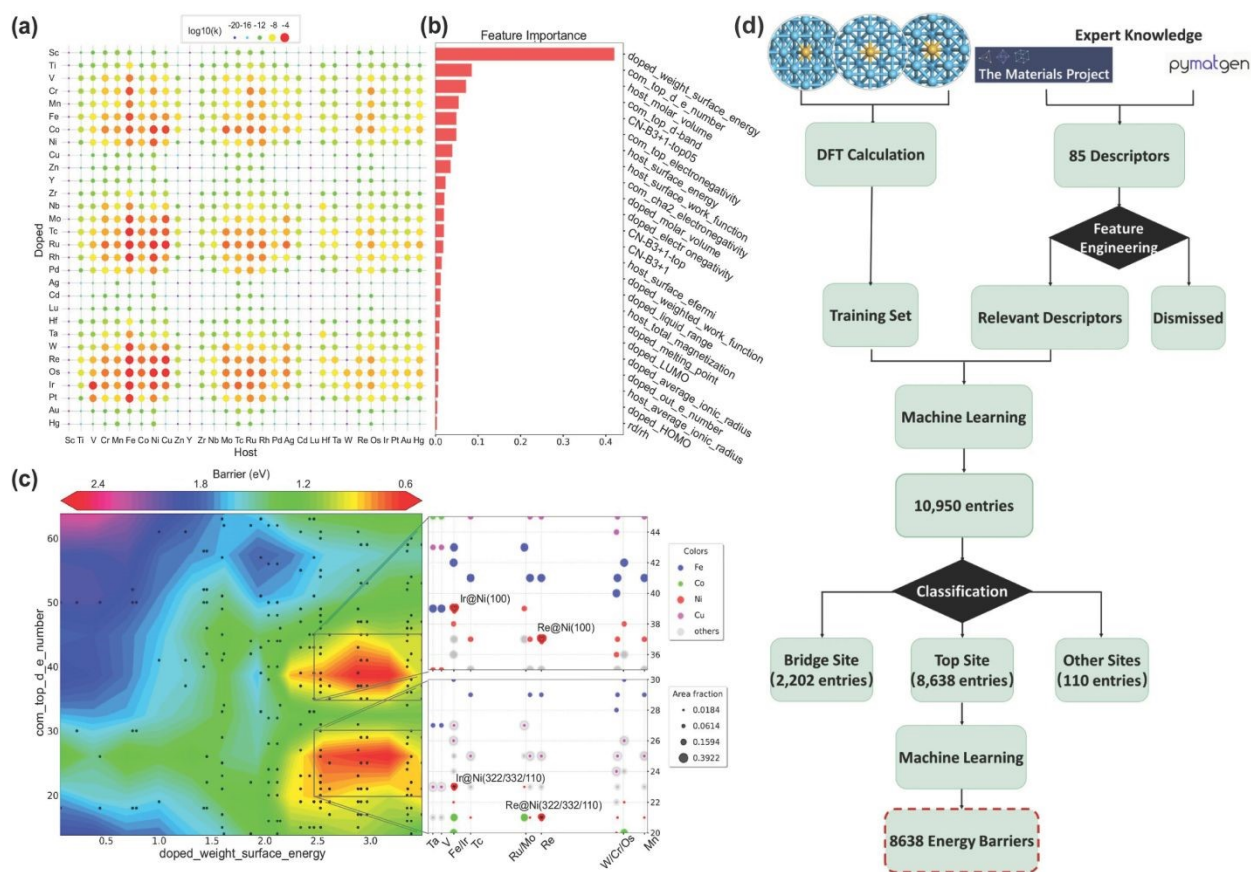


Figure 11. (a) C-H cleavage rates of all SAA surfaces at 450 °C. (b) Feature importance of 24 descriptors revealed from the ML model. (c) Two-dimensional volcano plot illustrating the relationship between the C-H dissociation barrier and top two descriptors of screened SAA surfaces. (d) Workflow of generating C-H cleavage barrier database on SAA surfaces, including performing DFT calculations, conducting feature engineering, developing ML models, and estimating energy barriers using ML models. (a)-(c) Reproduced from Ref.⁷⁹ with permission from Springer Nature, copyright 2024. (d) Reproduced from Ref.⁸⁰ with permission from Springer Nature, copyright 2025.

A very recent work by Feng et al.⁶⁴ combined DFT calculations with supervised ML to discover efficient SAA catalysts for alkane dehydrogenation. They first constructed 92 DFT-calculated methane C-H activation barriers across 23 SAA surfaces and performed feature selection to narrow down 23 features to 12 optimal features for training ML models. Bagging regression (BAR) model achieves the best accuracy of an RMSE value of 0.06 eV and was then used to screen 53 SAA candidates. Feature importance analysis indicates that the dehydrogenation step index (1-4, where 1 denotes the first dehydrogenation step), surface energy, and dopant lattice constant are dominant descriptors. The significant contribution of surface energy aligns well with the above studies, confirming its critical role in governing SAA

activity.^{63, 76, 79} ML predictions identified Ru/Cu(111) as a highly active catalyst for alkane dehydrogenation. DFT calculations confirm that Ru/Cu(111) is not only active for methane dehydrogenation, but also shows high reactivity for ethane, propane, and isobutane dehydrogenation. Microkinetic modeling further reveals that Ru/Cu(111) shows a high selectivity toward generating propylene from propane dehydrogenation. Overall, this work shows an effective ML and DFT framework to guide SAA design for alkane dehydrogenation, and identifies Ru/Cu(111) as a highly active and selective catalyst for C₁-C₄ activation.

Collectively, the above studies introduce the framework of applying ML models to the discovery of SAA catalysts for methane activation. Early work⁷⁶ established that simple regression models using elemental features reproduce methane dehydrogenation intermediate adsorption energies, laying the groundwork of data-driven high-throughput screening. Subsequent work^{77, 78} combined ML models with physics-informed principles to evaluate catalytic performances of a vast chemical space of SAA catalysts, even extending methane dehydrogenation to other alkanes. Beyond ML model development, feature analyses consistently inform two key descriptors, i.e., the group of periodic table and surface energy of dopant elements, in governing SAA reactivity. To summarize, ML has become an emergent tool in accelerating SAA catalyst discovery, which enables efficient exploration of structural and compositional spaces, and eventually guides experimental efforts.

Meanwhile, ML models for SAA discovery exhibit distinct trade-offs in terms of dataset size, computational efficiency, and transferability. Tree-based regression models, such as ETR and GBR, are highly efficient for predicting quantities, such as adsorption energies, and can be trained on relatively small datasets (on the order of ~100 DFT datapoints). Their negligible computational cost makes them attractive for rapid screening. However, they offer limited transferability and are generally less reliable when extrapolating beyond the training domain. In contrast, the SISSO approach typically relies on larger datasets, often comprising hundreds of DFT datapoints, but delivers explicit, low-dimensional, and interpretable descriptors. These descriptors help uncover the underlying physicochemical factors governing catalyst stability and activity, thereby providing transferable design principles for SAA catalysts. Supervised models enable large-scale ranking of thousands of candidate SAAs based on predicted activation barriers, although their reliability depends on rigorous out-of-sample validation and targeted DFT re-evaluations to ensure robustness and transferability. More recently, machine learning



interatomic potentials (MLIPs) have emerged as the most data-intensive approach, often requiring thousands of DFT datapoints for training. Despite this high cost, MLIPs make it possible to perform finite-temperature MD simulations and capture surface dynamics under experimentally relevant conditions.

4. Computational Efforts in SAAs for Activating Other Alkanes

Beyond the chemistry of methane activation, researchers have applied both DFT calculations and ML models to understand reactivity of SAA catalysts for activating other alkanes, such as ethane and propane. In this section, we summarize recent efforts of exploring SAA catalysts for dehydrogenation of alkanes other than methane, where additional C-H bond breaking and reaction intermediates introduce mechanistic complexity.^{27, 29, 61, 62, 65, 120, 121} Zhang et al.⁶⁵ systematically screened SAAs with Co, Ir, Ni, Pd, and Pt dopants embedded in surface layer of Cu, Ag, and Au host metals for ethane dehydrogenation. DFT and microkinetic modeling reveal that the reactivity of ethane dehydrogenation to ethylene correlates with: 1) $^*\text{C}_2\text{H}_4$ desorption energy that an easier desorption leads to a lower activity, and 2) $^*\text{C}_2\text{H}_5$ adsorption energy that a weaker adsorption leads to a higher selectivity. Across all studied SAA surfaces, $^*\text{C}_2\text{H}_4$ desorption is kinetically more favorable than further dehydrogenation and C-C bond breaking. Ten SAAs (Co/Cu, Ni/Cu, Pd/Cu, Pt/Cu, Ir/Ag, Ni/Ag, Pd/Ag, Pt/Ag, Ni/Au, Pd/Au) favor selective ethylene formation, and Ni/Cu SAA exhibits the best activity and selectivity, outperforming pure Pd and Pt catalysts.

In addition to dehydrogenation of C_2 hydrocarbons, computational efforts of designing SAA catalysts have been extended to C_3 chemicals. Cao et al.⁶¹ studied propane dehydrogenation on a single-Pd-doped Cu_{55} nanoparticle ($\text{Pd}_1/\text{Cu}_{55}$), a three-Pd-doped Cu_{55} nanoparticle ($\text{Pd}_3/\text{Cu}_{55}$), and a pure Cu_{55} nanoparticle (Figure 12). They found that propane binds weakly via physisorption on all three nanoparticles and the first C-H activation step is the rate-limiting step with a barrier of 1.06 eV on $\text{Pd}_1/\text{Cu}_{55}$, approximately 0.25 eV lower than on a pure Cu_{55} nanocluster. $^*\text{H}$ diffusion is kinetically favorable with a reaction barrier of 0.16 eV, leading to favorable H_2 formation. Subsequent dehydrogenation of $^*\text{C}_3\text{H}_7$ to propylene has a surmountable reaction barrier of 0.6 eV, while further C-H activation of propylene (1.16-1.43 eV) and C-C bond cleavage (2.56 eV) are kinetically unfavorable, suggesting high selectivity toward propylene formation. Introducing two additional Pd atoms only slightly lowers the initial



dehydrogenation barrier but impedes *H diffusion and propylene formation, indicating that the formation of isolated active sites in SAA enables both high activity and selectivity. AIMD further shows that the Pd_1/Cu_{55} nanoparticle is thermodynamically stable at a temperature of 500 K. Later, the authors extended the Cu_{55} nanocluster host to an extended $Cu(111)$ surface, forming a $Pd/Cu(111)$ SAA in a similar DFT work.¹²⁰ The results show a systematic d -band center upshift when increasing the number of Pd dopants, which strengthens adsorbate binding strength and reduce the first C-H activation barrier from 1.65 eV of a pure $Cu(111)$ to 1.43 eV of $Pd_1/Cu(111)$ and 1.13 eV of $Pd_3/Cu(111)$. C-H activation usually occurs around the active Pd sites and the dissociated *H migrates to adjacent Cu-Cu bridge sites to release Pd active sites and enable favorable further dehydrogenation steps. Even though multiple Pd dopants might improve activity of the initial dehydrogenation step, they also overbind intermediates and lead to coke formation, consistent with their previous conclusions on Cu nanoclusters.⁶¹ To summarize, the above studies demonstrate that single Pd dopants in the surface layer of Cu enhance selective C-H activation in propane to propylene. Hu and Cao¹²¹ extended this work by integrating DFT-calculated energetics with *in silico* vibrational spectroscopy, i.e., Infrared and Raman spectroscopies, to identify possible intermediates and elucidate reaction pathways on $Pd/Cu(111)$ with parallel and perpendicular propane adsorption sites (Figure 12). This work demonstrates the importance of using vibrational spectroscopy for investigating reaction mechanisms of long-chain alkane dehydrogenation, in which multiple competing pathways exhibit similar adsorption configurations and energetics.

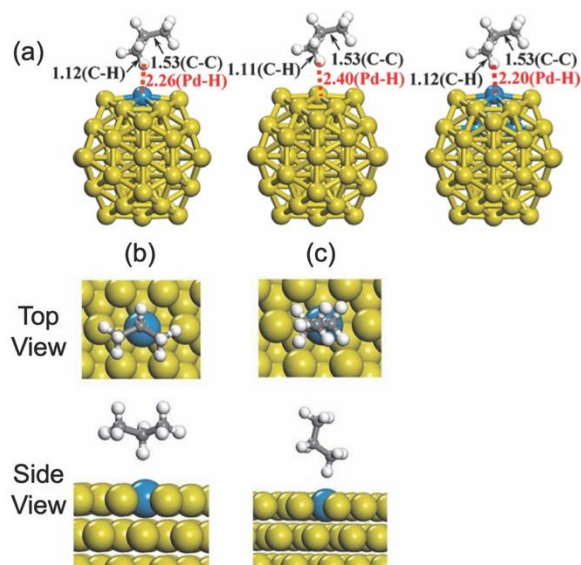


Figure 12. (a) Optimized structures of propane adsorption on a Pd₁/Cu₅₅ nanoparticle, a pure Cu₅₅ nanoparticle, and a Pd₃/Cu₅₅ nanoparticle. Top and side views of propane adsorption on Pd/Cu(111) with (b) parallel and (c) perpendicular configurations. (a) Reproduced from Ref.⁶¹ with permission from American Chemical Society, copyright 2014. (b-c) Reproduced from Ref.¹²⁰ with permission from Royal Society of Chemistry, copyright 2016.

Sun et al.²⁷ focused on the same reaction of propane dehydrogenation, but on a Pt/Cu SAA. They showed that incorporation of single Pt atoms on Cu catalysts breaks the scaling relationship for propane dehydrogenation,¹²² due to the significantly reduced binding strength of propene. In addition, the first two C-H activation barriers on Pt/Cu SAA are similar to those on a pure Pt(111). However, further dehydrogenation is suppressed on Pt/Cu SAA with high reaction barriers of above 2 eV, which are much higher than those on pure Pt catalysts. Meanwhile, they discovered that Pt/Ag SAA exhibits similar C-H activation barriers of propane dehydrogenation, but is not stable in the form of SAA. In a separate work, Hannagan et al.²⁹ investigated Rh/Cu(111) SAA for propane dehydrogenation and found that the first C-H activation barrier can be reduced to 0.57 eV, compared to 1.39 eV on Cu(111), 0.68 eV on Pt(111), and 0.63 eV on Rh(111), highlighting its superior activity. In addition, reaction barrier of further dehydrogenation step to *C₃H₆ on Rh/Cu(111) is extremely low, i.e., 0.1 eV (Figure 13), leading to propene formation. The superior activity and selectivity of Rh/Cu(111) SAA for propane to propene conversion was experimentally confirmed in the same work.

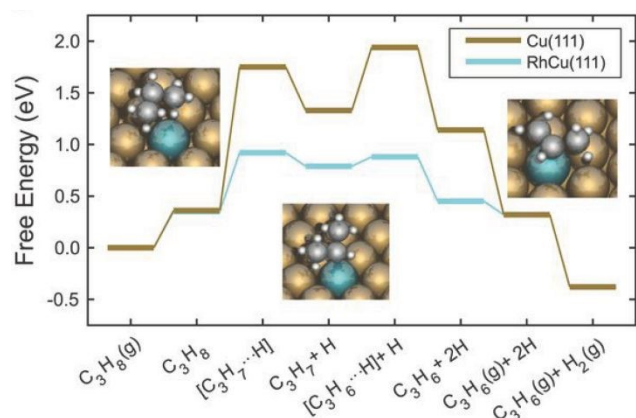


Figure 13. Energy profile of Rh/Cu(111) SAA and Cu(111) for propane dehydrogenation to propene. Energies are referenced to the clean slabs and a gas-phase C₃H₈. H denotes a H atom adsorbed on the surfaces. Reproduced from Ref.²⁹ with permission from AAAS, copyright 2021.

Bunting et al.⁶² combined DFT calculations, ML-trained interatomic potentials, and molecular dynamics (MD) simulations to perform a systematic study of the reactivity of Rh/Cu



and Pd/Cu SAAs for propane dehydrogenation (Figure 14). They first trained equivariant neural-network interatomic potentials (NequIP) using around 9000 DFT single-point calculations per SAA, generated from MD trajectories and transmutation Monte Carlo swaps over a wide temperature range of 200 to 1200 K. These ML-trained interatomic potentials enable large-scale MD simulations of a 3-nm Wulff-constructed Cu nanoparticle at experimentally relevant temperatures. Site-specific free energy pathways for C-H activation and propene and H₂ desorption were then proposed by combining DFT calculations and microkinetic modeling. MD simulations reveal that Rh dopants preferentially reside on the (111) facet, while Pd dopants exhibit broader distributions among multiple facets, including undercoordinated sites, which are much more reactive for C-H cleavage. For both dopants, the (111) terrace sites exhibit the lowest activity for propane dehydrogenation. Therefore, accounting for the dynamic behaviors leads to activity predictions that deviate by orders of magnitude from those simply using static (111) facet, which typically overestimates Rh/Cu(111) activity while underestimating Pd/Cu(111) activity.

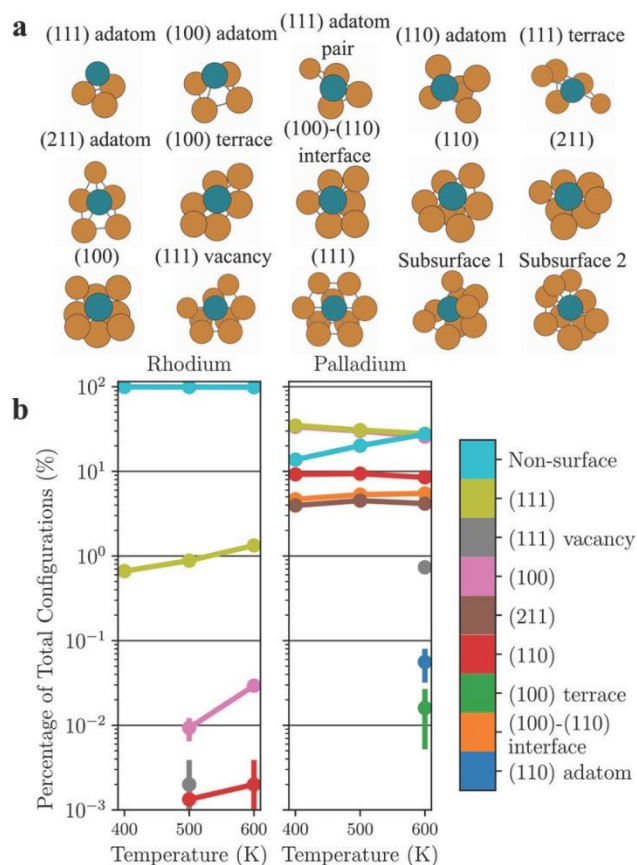


Figure 14. (a) Representative structures of 13 possible surface and two subsurface dopant sites for Cu-based SAAs. (b) Probability of dopant occupation at each site, obtained from MD simulations and transmutation Monte Carlo simulations using the ML-trained interatomic potentials. Surface sites are color-coded according to their classification and all non-surface sites are grouped into the non-surface category. Reproduced from Ref.⁶² with permission from American Chemical Society, copyright 2023.

The multi-scale computational tools discussed in Sections 2-4 play distinct yet complementary roles in the systematic design of SAA catalysts. DFT establishes the mechanistic foundation by identifying active sites and quantifying reaction energies and activation barriers on SAAs, thereby rationalizing the dopant-host synergy. For example, DFT studies show that isolated dopant sites can substantially reduce the first C-H activation barrier on Pt/Cu(111) relative to Cu(111), providing a microscopic explanation for enhanced low-temperature activity.²⁸ To bridge these static 0 K predictions with experimental conditions, AIMD captures finite-temperature effects, surface dynamics, and entropic contributions at elevated temperatures. This is illustrated by studies of temperature-dependent C-H activation of CHD₃ on Pt/Cu(111) SAA⁵³ and the thermal stability of Pd₁/Cu₅₅ nanoparticles.⁶¹ Microkinetic modeling then translates these DFT-derived energetics into macroscopic observables such as rates and selectivity, enabling direct comparison with experimental performance. Microkinetic modeling of ethane dehydrogenation over Ni/Cu SAAs has been used to predict ethylene yields and assess selectivity trends.⁶⁵ Despite their mechanistic rigor, first-principles methods are computationally demanding and therefore limited in scalability when exploring the broad compositional and structural space. Consequently, ML emerges as a powerful strategy to address these limitations by leveraging DFT-generated datasets to enable high-throughput screening and to uncover transferable design principles across vast chemical space. Such ML-driven approaches have successfully identified novel, experimentally viable candidates for methane activation, including Ir/Ni(111) and Re/Ni(111).⁷⁹

5. Conclusions and Outlook

This review provides a summary of recent computational progress in understanding and designing SAA catalysts for activation of methane and other light alkanes. We first presented first-principles studies, with DFT calculations, AIMD simulations, and microkinetic modeling, across extensive dopant-host SAA combinations. These studies revealed several mechanistic



insights into methane and other alkane activation on SAA catalysts: (i) transition states of the initial C-H cleavage are localized around the active dopant region, yielding activation barriers similar to those on the pure dopant metal; (ii) less reactive host atoms moderately bind intermediate species, suppressing further dehydrogenation and thus avoiding coke formation; and (iii) the synergy between dopant and host metal enhances selective C-C coupling towards multi-carbon hydrocarbons. We next summarized the accelerated SAA catalyst design work with a powerful computational tool, ML, which has transformed SAA discovery from case-by-case exploration to high-throughput screening through accurate predictions of adsorption energies and activation barriers using interpretable descriptors. Finally, we extended the review from methane activation to activation of multi-carbon alkanes.

Across computational studies, the most commonly adopted activity descriptor for methane activation is the reaction barrier associated with the first C-H bond cleavage. Among widely studied host metals (Cu, Ag, and Au) and dopants (Ni, Pd, Pt, and Rh), Rh-doped SAAs consistently exhibit the lowest activation barriers, with representative values of ~ 0.55 – 0.64 eV reported for Rh/Ag(111), Rh/Au(111), and Rh/Cu(111). When full dehydrogenation pathways are studied on Cu-based SAAs, Rh/Cu(111) is repeatedly identified as one of the most reactive candidates, which benefits from dopant-host synergy that mitigates excessive dehydrogenation compared with pure dopant metals. Beyond these typical SAAs, Ir-doped SAAs have been predicted to exhibit exceptionally high activity on selected facets, such as Ir/Pt(110), where a near-zero initial barrier has been reported. However, such studies often focus solely on the first C-H bond cleavage and therefore require further evaluation of subsequent dehydrogenation steps and possible coking susceptibility. Finally, recent data-driven screening efforts have broadened the design space for methane decomposition catalysts, identifying promising systems, including Ni-based SAAs and emerging Cu-based candidates, such as Ru/Cu(111), that combine high activity with improved resistance to over-dehydrogenation.

Looking forward, numerous opportunities remain to further advance SAA catalysis. First, the accessible structural and compositional space should extend beyond the conventional paradigm of dispersing an active dopant within an inert host. Systematic exploration of underexplored dopant-host combinations, non-traditional catalytic transition metals, and stepped or defect-rich facets may reveal novel structure-composition-property relationships. To make such expansion both practical and accurate, the field should evolve from conventional high-



throughput DFT screening toward active-learning workflows with uncertainty quantification. Such approaches can prioritize the most informative SAA candidates for DFT validation and thus accelerate discovery in underexplored chemical spaces. Second, improving transferability will require the establishment of benchmark “anchor sets”, i.e., shared reference calculations performed on a small, agreed-upon list of SAAs and elementary steps computed using consistent settings. These anchor sets would enable cross-study normalization and more reliable comparisons of activity. Third, there is a critical need for general, physics-informed descriptors and design principles that remain robust across diverse dopants, hosts, and facets. To achieve this, advanced quantum mechanical simulations beyond standard DFT, such as embedded correlated wavefunction theory,^{44–46, 123–125} can enable a more rigorous description of electronic structures and thus yield more reliable descriptors for SAA catalysis. In parallel, advanced ML frameworks with explicit uncertainty quantification can improve robustness and generalizability across different alkane chemistries. Finally, realizing these goals will benefit from collaborative data ecosystems. The development of open, standardized SAA databases and benchmarking protocols would enable cross-validation of models and ensure that descriptors developed for methane activation remain transferable to longer-chain hydrocarbon chemistry. Overall, the tight integration of first-principles theory, data-efficient ML, and community data sharing will be essential for translating computational insights into industrially relevant, low-carbon alkane valorization using SAA catalysts.

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Supporting Information

No supporting information.

Conflicts of interests

There are no conflicts of interest to declare.

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Data Availability Statement

No primary research results, software or code have been included and no new data were generated or analyzed as part of this review.

