

# Methane Activation on Single-Atom Ir-doped Metal Nanoparticles from First-principles

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**Table S1:** Transition state information on the pure metal surface.

		rigid				relaxed			
		$d_{MC}$	$R_{CH}$	$\theta$	$E_b$	$d_{MC}$	$R_{CH}$	$\theta$	$E_b$
		(Å)	(Å)	(°)	(eV)	(Å)	(Å)	(°)	(eV)
<b>Co</b>	<b>100</b>	2.093	1.613	132	0.851	2.067	1.611	132	0.791
	<b>110</b>	2.099	1.662	125	0.999	2.058	1.681	128	0.894
	<b>111</b>	2.147	1.614	128	1.082	2.111	1.732	125	0.993
<b>Rh</b>	<b>100</b>	2.223	1.57	130	0.674	2.205	1.556	130	0.596
	<b>110</b>	2.205	1.625	127	0.716	2.203	1.598	131	0.653
	<b>111</b>	2.147	1.614	128	1.082	2.111	1.732	125	0.993
<b>Ir</b>	<b>100</b>	2.283	1.452	133	0.555	2.283	1.441	133	0.463
	<b>110</b>	2.263	1.568	127	0.477	2.25	1.525	127	0.374
	<b>111</b>	2.297	1.581	129	0.892	2.259	1.49	132	0.716
<b>Ni</b>	<b>100</b>	2.065	1.629	126	0.934	2.025	1.643	127	0.807
	<b>110</b>	2.036	1.642	126	0.761	2.022	1.658	129	0.717
	<b>111</b>	2.108	1.696	127	1.043	2.057	1.547	136	0.886
<b>Pd</b>	<b>100</b>	2.174	1.634	132	0.740	2.157	1.608	132	0.644
	<b>110</b>	2.170	1.587	134	0.722	2.157	1.638	132	0.692
	<b>111</b>	2.204	1.687	131	0.873	2.180	1.657	130	0.819
<b>Pt</b>	<b>100</b>	2.267	1.449	135	0.604	2.231	1.414	135	0.447
	<b>110</b>	2.240	1.477	132	0.383	2.234	1.459	132	0.346
	<b>111</b>	2.257	1.532	131	0.845	2.224	1.524	129	0.734

**Table S2:** Information on the transition state of the alloy surface.

		relaxed				rigid				
		$E_b$	$R_{CH}$	$d_{MC}$	$\theta$	$E_b$	$R_{CH}$	$d_{MC}$	$\theta$	$d_{Ir-Ir'}$
		(eV)	(Å)	(Å)	(°)	(eV)	(Å)	(Å)	(°)	(Å)
<b>Ir@Rh</b>	<b>100</b>	0.506	1.420	2.277	132	0.613	1.43	2.30	132	0.131
	<b>110</b>	0.437	1.474	2.250	119	0.541	1.52	2.26	124	0.108
	<b>111</b>	0.697	1.483	2.621	129	0.833	1.52	2.30	130	0.200
<b>Ir@Ni</b>	<b>100</b>	0.488	1.447	2.268	133	0.569	1.45	2.30	133	0.130
	<b>110</b>	0.481	1.482	2.228	131	0.578	1.52	2.24	136	0.123
	<b>111</b>	0.644	1.507	2.258	128	0.811	1.52	2.32	133	0.198
<b>Ir@Pd</b>	<b>100</b>	0.331	1.360	2.275	133	0.529	1.47	2.32	132	0.192
	<b>110</b>	0.100	1.450	2.229	122	0.240	1.49	2.24	125	0.098
	<b>111</b>	0.290	1.417	2.263	128	0.539	1.51	2.28	131	0.234

<b>Ir@Pt</b>	<b>100</b>	0.237	1.392	2.259	133	0.401	1.40	2.30	133	0.185
	<b>110</b>	0.014	1.430	2.233	119	0.100	1.51	2.24	121	0.089
	<b>111</b>	0.382	1.485	2.229	128	0.633	1.52	2.28	131	0.271
<b>Ir@Cu</b>	<b>100</b>	0.433	1.458	2.26	131	0.539	1.47	2.30	133	0.174
	<b>110</b>	0.335	1.461	2.212	137	0.402	1.50	2.23	133	0.133
	<b>111</b>	0.471	1.490	2.279	129	0.626	1.52	2.32	131	0.214
<b>Ir@Ag</b>	<b>100</b>	0.302	1.420	2.525	130	0.502	1.44	2.29	131	0.164
	<b>110</b>	0.114	1.401	2.222	134	0.176	1.43	2.24	133	0.110
	<b>111</b>	0.301	1.439	2.273	129	0.498	1.49	2.31	131	0.240

**Table S3:** Transition state Bader-charge analysis(e).

		<b>relaxed</b>		
		<b>CH<sub>3</sub></b>	<b>Ir</b>	<b>H</b>
<b>Ir@Rh</b>	<b>100</b>	-0.0554	0.0195	0.0602
	<b>110</b>	-0.0504	-0.0297	0.0712
	<b>111</b>	-0.0255	-0.101	0.0757
<b>Ir@Ni</b>	<b>100</b>	-0.0568	-0.247	0.0520
	<b>110</b>	-0.0578	-0.219	0.0500
	<b>111</b>	-0.0568	-0.284	0.0580
<b>Ir@Pd</b>	<b>100</b>	-0.0319	0.0607	0.0730
	<b>110</b>	-0.0166	0.0462	0.0807
	<b>111</b>	-0.0185	0.00144	0.0885
<b>Ir@Pt</b>	<b>100</b>	-0.0115	0.165	0.0889
	<b>110</b>	-0.0135	0.182	0.0797
	<b>111</b>	0.0258	0.135	0.107
<b>Ir@Cu</b>	<b>100</b>	-0.0345	-0.382	0.0272
	<b>110</b>	-0.0653	-0.313	0.0418
	<b>111</b>	-0.0551	-0.447	0.0509
<b>Ir@Ag</b>	<b>100</b>	-0.0340	-0.230	0.0398
	<b>110</b>	-0.0363	-0.216	0.0427
	<b>111</b>	-0.0722	-0.249	0.0548

**Table S4:** Surface energy of alloy crystal plane (J/m<sup>2</sup>).

		<b>E<sub>M</sub><sup>clean</sup></b>	<b>300K</b>	<b>500K</b>	<b>700K</b>
			<b>E<sub>surface</sub></b>	<b>E<sub>surface</sub></b>	<b>E<sub>surface</sub></b>
<b>Ir@Rh</b>	<b>100</b>	2.434	2.463	2.534	2.61
	<b>110</b>	2.457	2.472	2.522	2.576
	<b>111</b>	2.059	2.115	2.196	2.285
<b>Ir@Ni</b>	<b>100</b>	1.934	1.966	2.047	2.136
	<b>110</b>	2.090	2.110	2.168	2.231

	<b>111</b>	1.537	1.598	1.692	1.795
	<b>100</b>	1.682	1.694	1.761	1.834
<b>Ir@Pd</b>	<b>110</b>	1.702	1.701	1.749	1.800
	<b>111</b>	1.497	1.521	1.598	1.682
	<b>100</b>	1.937	1.932	1.998	2.070
<b>Ir@Pt</b>	<b>110</b>	1.979	1.958	2.005	2.055
	<b>111</b>	1.588	1.603	1.679	1.761

**Table S5:** Proportions of (100), (110) and (111) surfaces of pure metal nanoparticles under two different given pressures at T=500 K

		<b>100</b>	<b>110</b>	<b>111</b>
<b>Rh</b>	<b>P=1bar</b>	21%	11%	68%
	<b>P=10bar</b>	21%	10%	69%
<b>Ir</b>	<b>P=1bar</b>	20%	0%	80%
	<b>P=10bar</b>	19%	0%	81%
<b>Ni</b>	<b>P=1bar</b>	23%	0%	77%
	<b>P=10bar</b>	22.4%	0%	77.6%
<b>Pd</b>	<b>P=1bar</b>	26%	17%	57%
	<b>P=10bar</b>	26%	16%	58%
<b>Pt</b>	<b>P=1bar</b>	22%	5%	73%
	<b>P=10bar</b>	22%	4%	74%

**Table S6:** Proportions of (100), (110) and (111) surfaces of alloy metal nanoparticles under two different given pressures at T=500 K.

		<b>100</b>	<b>110</b>	<b>111</b>
<b>Ir@Rh</b>	<b>P=1bar</b>	22%	15%	63%
	<b>P=10bar</b>	22%	14%	64%
<b>Ir@Ni</b>	<b>P=1bar</b>	18%	0%	82%
	<b>P=10bar</b>	17%	0%	83%
<b>Ir@Pd</b>	<b>P=1bar</b>	24%	25%	51%
	<b>P=10bar</b>	24%	25%	51%

<b>Ir@Pt</b>	<b>P=1bar</b>	19.4%	5.6%	75%
	<b>P=10bar</b>	19.2%	4.4%	76.4%

**Table S7:** Proportions of (100), (110) and (111) surfaces of alloy metal nanoparticles under different temperatures at P=1bar.

	<b>300K</b>			<b>500K</b>			<b>700K</b>		
	<b>100</b>	<b>110</b>	<b>111</b>	<b>100</b>	<b>110</b>	<b>111</b>	<b>100</b>	<b>110</b>	<b>111</b>
<b>Ir@Rh</b>	22%	10%	68%	22%	15%	63%	22%	19%	59%
<b>Ir@Ni</b>	16%	0%	84%	18%	0%	82%	19%	0%	81%
<b>Ir@Pd</b>	24%	20%	56%	24%	25%	51%	24%	31%	45%
<b>Ir@Pt</b>	18%	0%	82%	19.4%	5.6%	75%	20%	11%	69%

**Table S8:** The pure metal activity(S<sup>-1</sup>).

<b>Rh</b>	<b>Ir</b>	<b>Ni</b>	<b>Pd</b>	<b>Pt</b>
20.168	19.330	14.405	17.551	19.759

**Table S9:** The alloy activity(S<sup>-1</sup>).

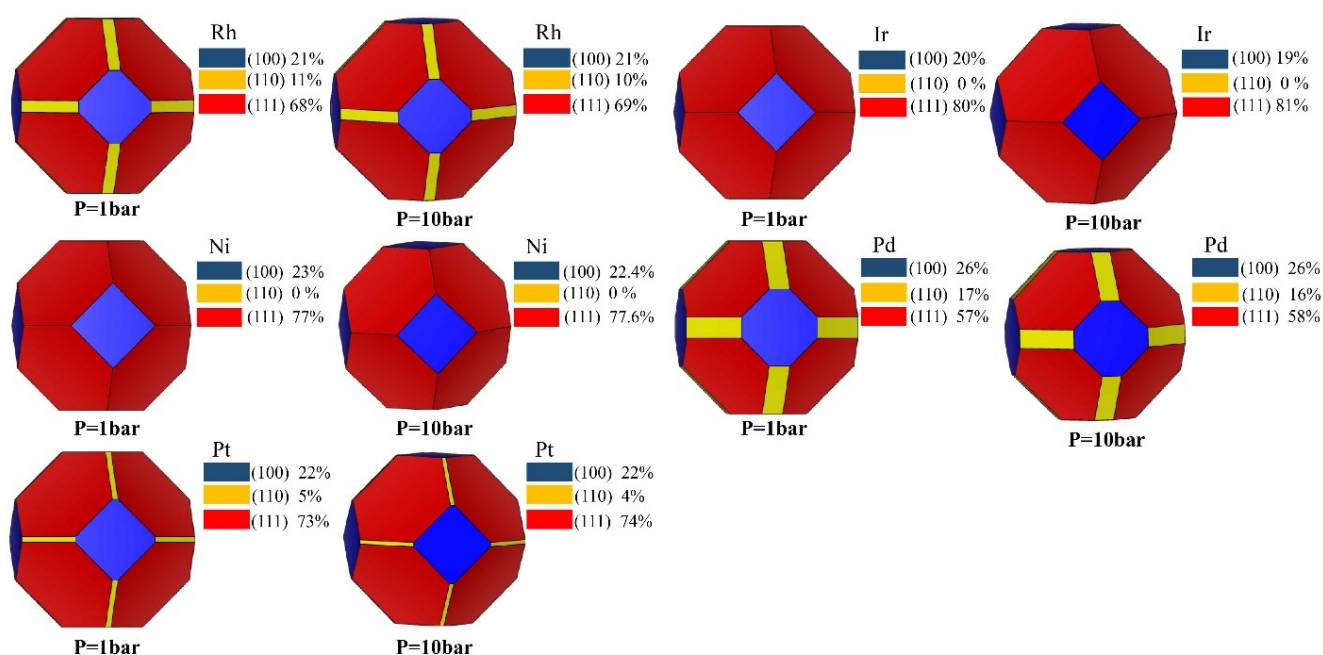
	<b>300K</b>	<b>500K</b>	<b>700K</b>
<b>Ir@Rh</b>	15.745	20.741	23.840
<b>Ir@Ni</b>	12.862	16.902	19.443
<b>Ir@Pd</b>	19.049	21.476	23.533
<b>Ir@Pt</b>	18.242	23.785	25.819

**Table S10:** The dissociation barrier of methane and adsorption energy of methyl on Ni(111) surface with and without the van der Waals correction.

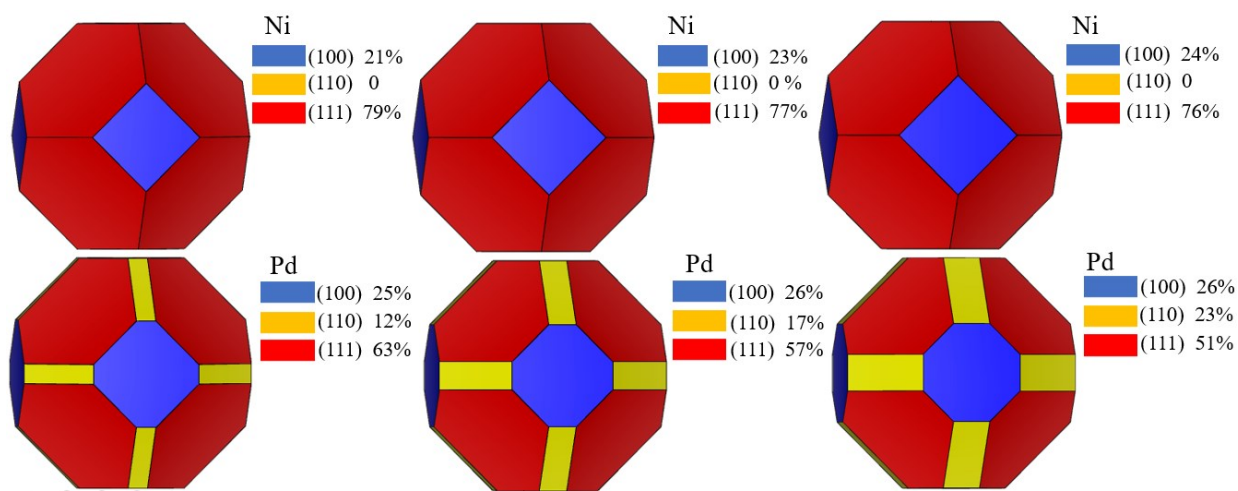
	<b>Uncorrected</b>	<b>Van der Waals correction</b>
<b>Dissociation barrier(E<sub>b</sub>/eV)</b>	0.886	0.575

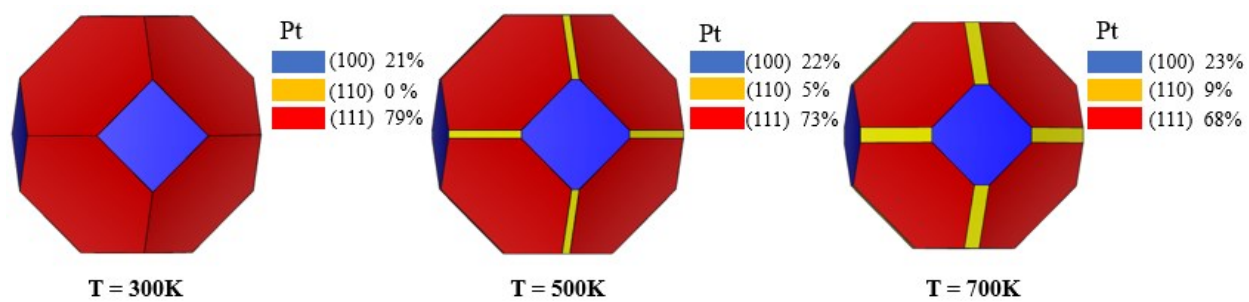
\* Using DFT calculations (DFT-D3), the energy barrier and the adsorption energy of methyl with and without van der Waals correction are shown in Table S10. With the van der Waals correction, it is found that the energy barrier is decreased from 0.886 eV to 0.575 eV. Compared with the previous works, it is found that the adsorption energy of methyl on Ni(111) surface is closed to those previous results, e.g., -2.24 eV obtained by Lai et al. [1], -1.97eV obtained by Wang et al. [2], -1.98 eV obtained by Zhu et al. [3], -2.60eV obtained by Upton et al. [4] and -1.86 eV obtained by Wonchoba and Truhlar[5]. The van der Waals correction strengthens the adsorption energy of methyl on the Ni(111) surface.

**FigureS1:** Wulff structures of Ni, Pd, Pt, Rh and Ir metals at different pressures.

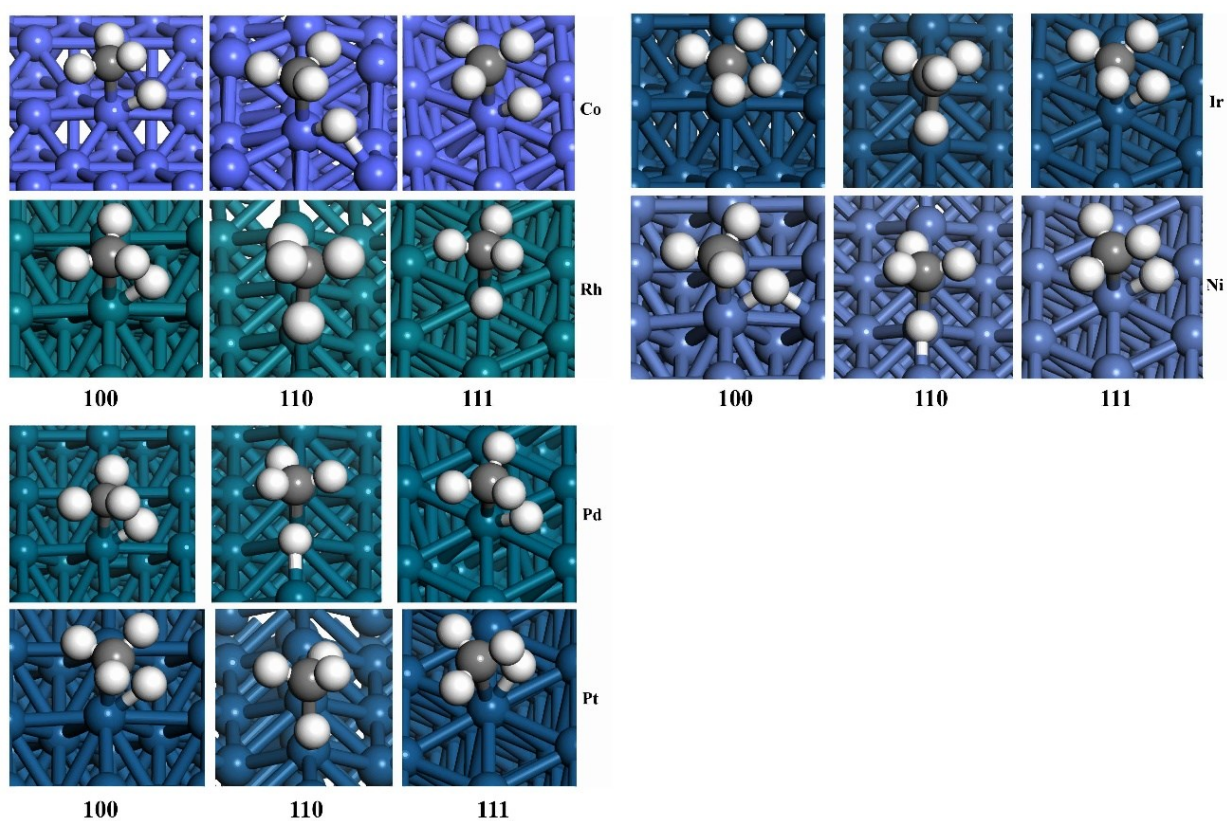


**FigureS2:** Wulff structures of Ni, Pd, Pt, Rh and Ir metals at different temperatures.



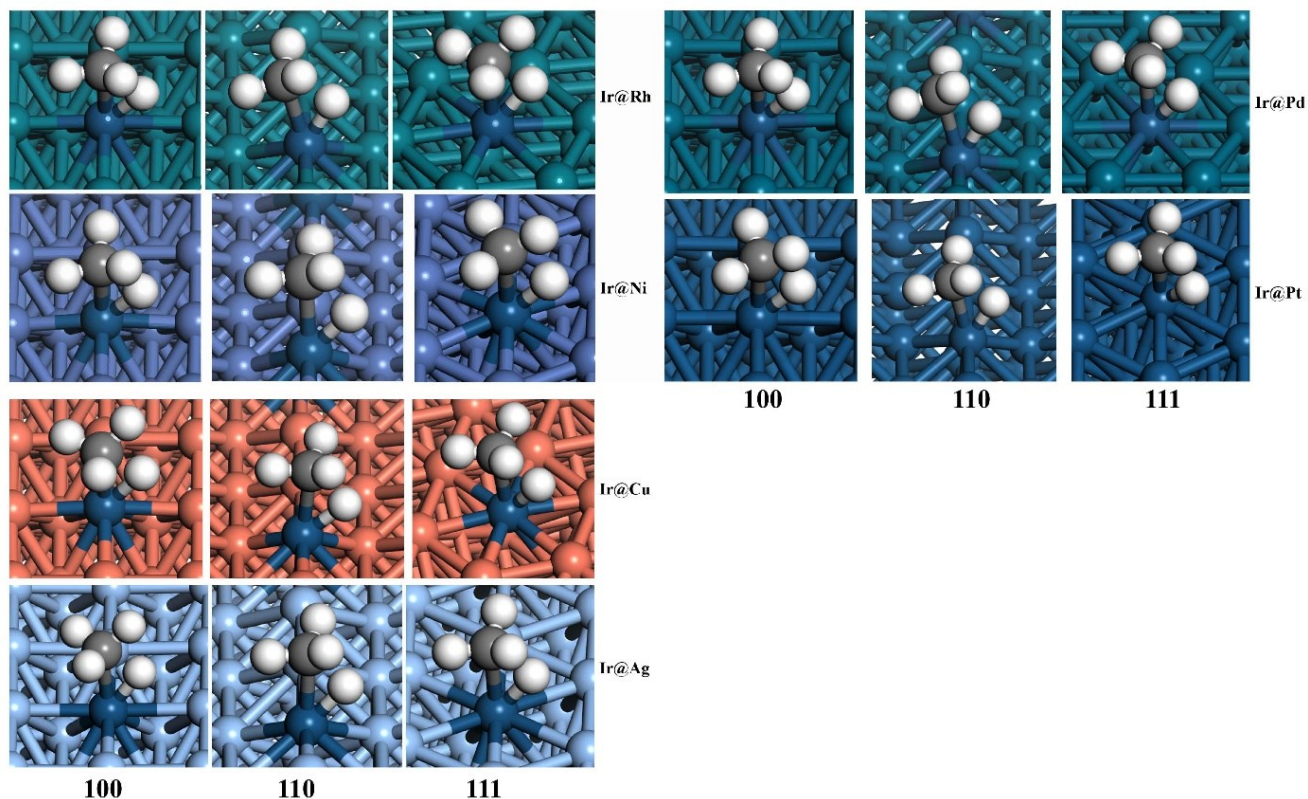


**Figure S3:** Transition states of methane activation on different pure metal surfaces including (100), (110) and (111) surfaces.

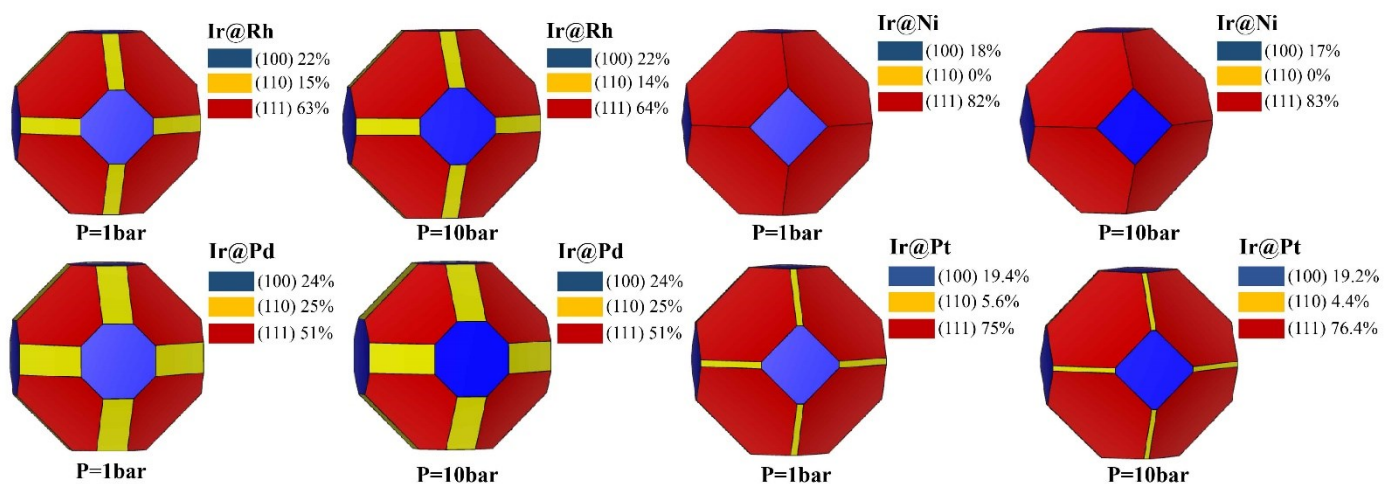




**Figure S4:** Transition states of methane activation on different alloy metal surfaces including (100), (110) and (111) surfaces.

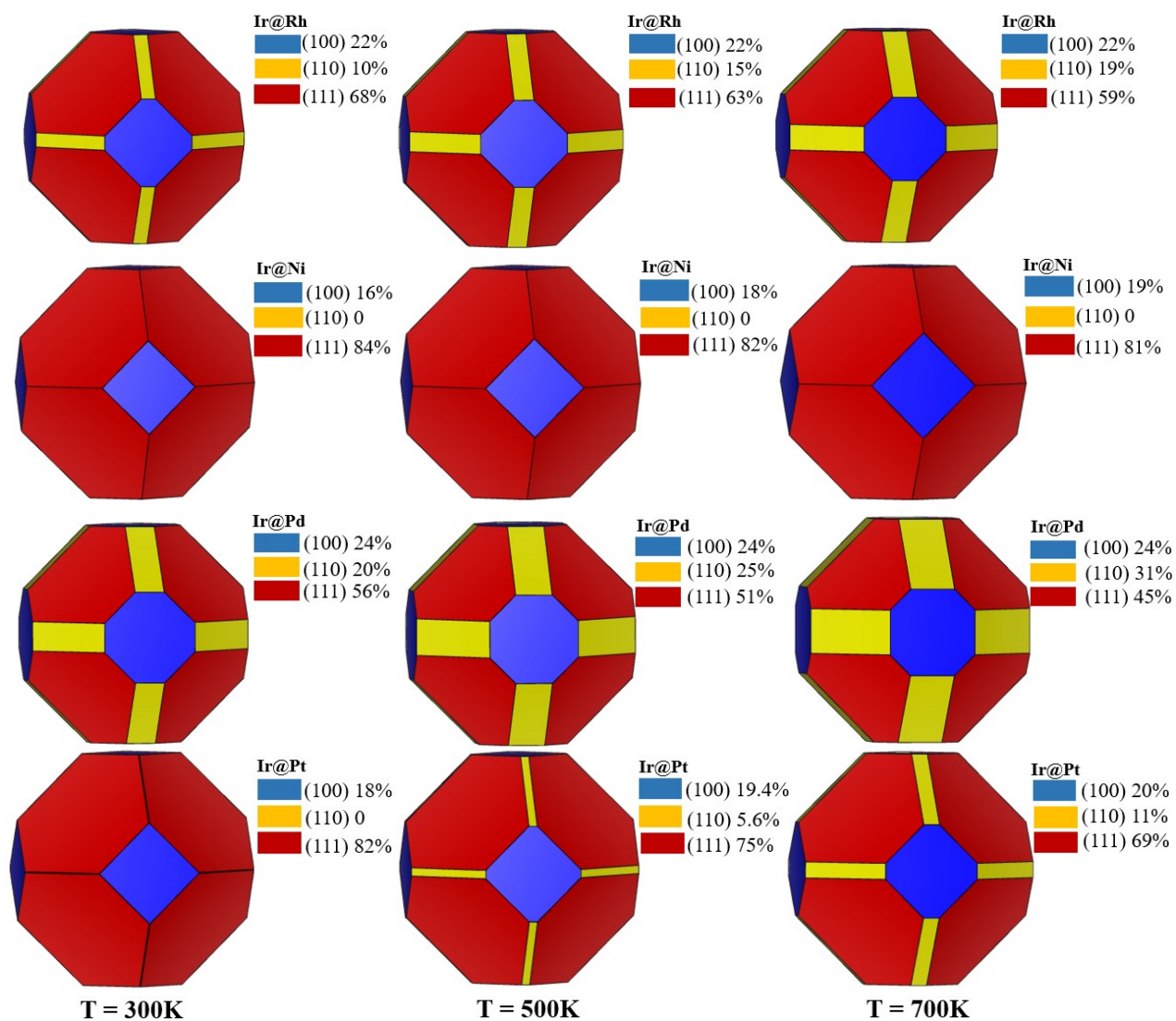


**FigureS5:** Wulff structures of Ir@M alloy at different pressures.





**FigureS6:** Wulff structures of Ir@M alloy at different temperatures.



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