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Lowering C-H Bond Activation Barrier of Methane by Means of SAC@Cu(111): Periodic DFT Investigations

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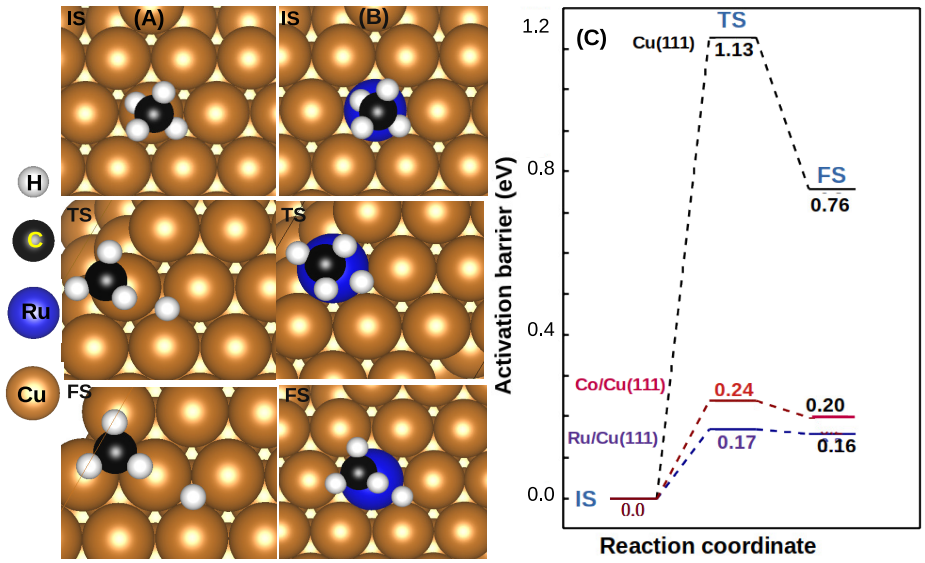

Fig. 1 Chemisorption and physisorption of methane on various SACs in term of adsorption energy as a function of (A) C-H bond length and (B) M-C bond length

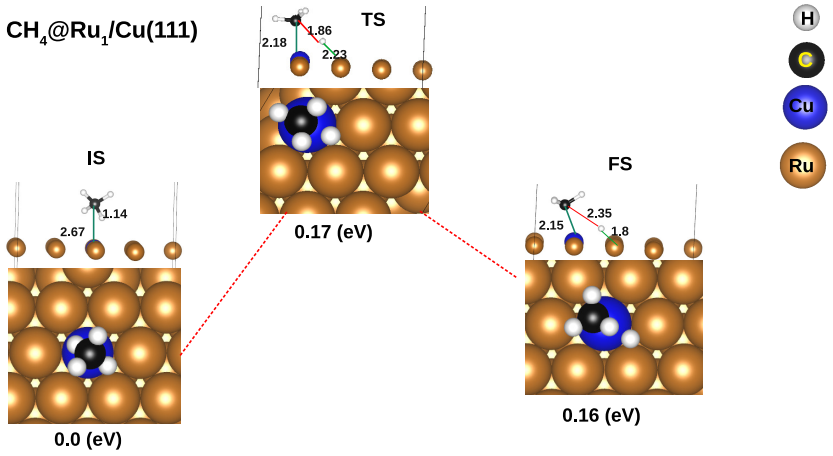

Fig. 2 Top and side view for the first C-H bond dissociation ($CH_4 \rightarrow CH_3 + H$) reaction path on Ru/Cu(111) SAC

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Table 1 M-C, C-H bond length and corresponding adsorption energy (eV) for TM/Cu(111) surfaces

Dopant(TM_1)	b_{C-H} (Å)	b_{M-C} (Å)	E_{ads}(eV)	E_{act}	E_{act}(ZPC)	E_{rec}(eV)			
Group	4	5	6	7	8	9	10	11	12
				3d					
TM_1/dopant	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
C-H (Å)	1.121	1.124	1.124	1.124	1.135	1.130	1.104	1.103	1.101
M-C (Å)	2.51	2.46	2.44	2.4	2.56	2.67	3.0	3.14	3.2
E_{ads}	-0.63	-0.62	-0.58	-0.53	-0.47	-0.41	-0.35	-0.34	-0.27
				4d					
TM_1/dopant	Zr		Mo	Tc	Ru	Rh	Pd	Ag	
C-H (Å)	1.117		1.126	1.122	1.141	1.123	1.104	1.101	
M-C (Å)	2.71		2.57	2.58	2.6	2.9	3.1	3.2	
E_{ads}	-0.74		-0.64	0.57	-0.51	-0.40	-0.34	-0.32	
				5d					
TM_1/dopant						Ir	Pt	Au	
C-H (Å)						1.102	1.101	1.101	
M-C (Å)						3.3	3.4	3.1	
E_{ads}						-0.39	-0.35	-0.31	

Table 2 Mulliken charges on the dopant and Cu atom of SACs and Cu(111), and carbon atom of methane before and after methane adsorption on SACs and Cu(111) surfaces.

Dopant element	Charge on dopant@SAC	charge on dopant when CH_4 is adsorbed	charge on C atom	group
Ti	0.52	0.32	-1.19	
V	0.27	0.08	-1.17	
Cr	-0.14	-0.20	-1.16	
Mn	-0.28	-0.03	-1.16	3d
Fe	-0.34	-0.13	-1.12	
Co	-0.36	-0.16	-1.10	
Ni	-0.29	-0.09	-1.13	
Cu	0.15	-0.01	-1.13	
Mo	-0.54	-0.58	-1.18	
Ru	-0.64	-0.65	-1.15	4d
Rh	-0.59	-0.65	-1.16	
CH_4 molecule	-	-	-1.14	