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Supporting information

Chemisorbed oxygen atom on the activation of C-H bond in methane: A Rh model study

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Table S1

	Site	O	H	CH_3	CH_2
Ad-row	E-B	-5.69(-5.40) [b)]	-2.88(-2.76) [b)]	-2.42(-2.31) [b)]	-4.68(-4.63) [b)]
	E-T	N [a)]	N [a)]	-2.17(-2.15) [b)]	--
	3H1	N [a)]	-2.77	N [a)]	-4.63
	3H2	-4.16	-2.55	N [a)]	-4.45
	Br.	--	-2.77	--	N [a)]
	T-T	-4.91	---	--	---
	T-B	-4.89	-2.55	--	-4.48
	T-FCC	-4.59	-2.45	--	-4.26
Ad-atom	E-B	-4.80 (-4.85)[b)]	-2.87 (-2.83)[b)]	---	-4.52 (-4.48) [b)]
	E-T	-4.62 (-4.64) [b)]	--- (-2.00) [b)]	-2.25 (-2.27) [b)]	-3.53 (-3.55) [b)]
	3H	--	-2.72 (-2.65) [b)]	-2.17	-4.41
	T-T	--	N [a)]	-1.71(-1.74) [b)]	N [a)]
	T-B	N [a)]	-2.87	-2.12 (-1.64) [b)]	-4.40
	T-FCC	-4.57	-2.58	-2.10	-4.39 (-4.87)

Note: EB means Edge-bridge, KB mean Kink-bridge, K3H means Kink-3H, E3H means the Edge-3H, T-T means terrace-top site, T-B means terrace-bridge site, and T-FCC means terrace-fcc site.

N [a)] means the adsorbated species dose not adsorb at the given site and moves to a more stable adsorption site.

[b)] DFT results of p(3x3) model.

Table S2

	CH_4	CH_3	CH_2	
111	-0.12	-2.66	-4.90	Ref.[1]
100	-0.16	-2.75	-5.34	Ref.[1]
110	-0.62	-3.33	-5.58	Ref.[1]
211	---	-3.05	-5.23	Ref.[2]

Table S3

	111	100	110	211	kink	Ad-row	Ad-atom
Site	HCP	4H	LB	EB	EB	E3H	E3H
$E_{ad(C)/eV}$	-7.28	-8.06	-7.79	-7.89	-7.63	-7.61	-7.82

Table S4

	CH_4				CH_3				
	Rh		O/Rh		Rh		O/Rh		
	E_a	ΔH	E_a	ΔH	E_a	ΔH	E_a	ΔH	
(111)	0.69				0.42				Ref.[3]
	0.73		1.10	0.26					Ref.[4]
	0.82	-0.12			0.55				Ref.[1]
	0.60	-0.07			0.47	-0.27			Ref.[2]
	0.67	0.02							Ref.[5]
(100)	0.65				0.33				Ref.[1]
(110)	0.70	-0.14			0.32				Ref.[2]
(211)	0.50				0.40				Ref.[3]
	0.30								Ref.[5]
Ad-row	0.48				0.35				Ref.[3]
Ad-atom	0.46		1.22	-0.49	0.63				Ref.[3]
	0.41								Ref.[4]
Kink	0.20								Ref.[5]

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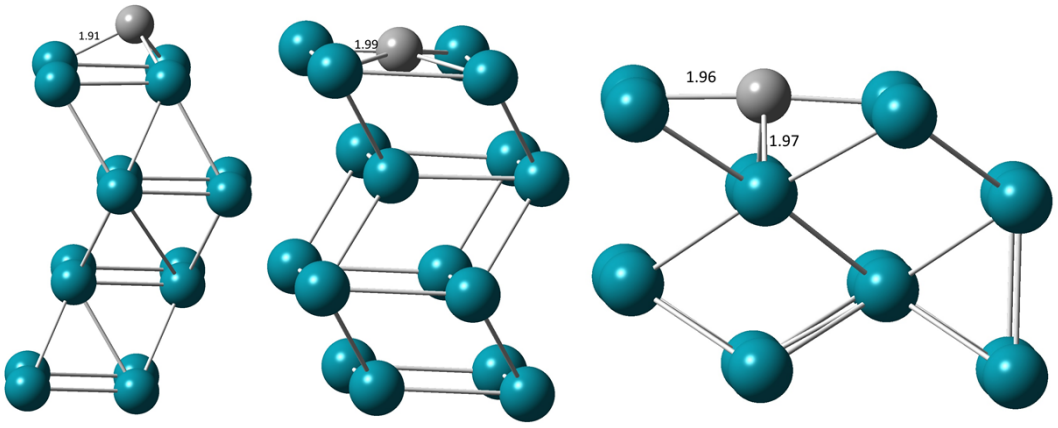
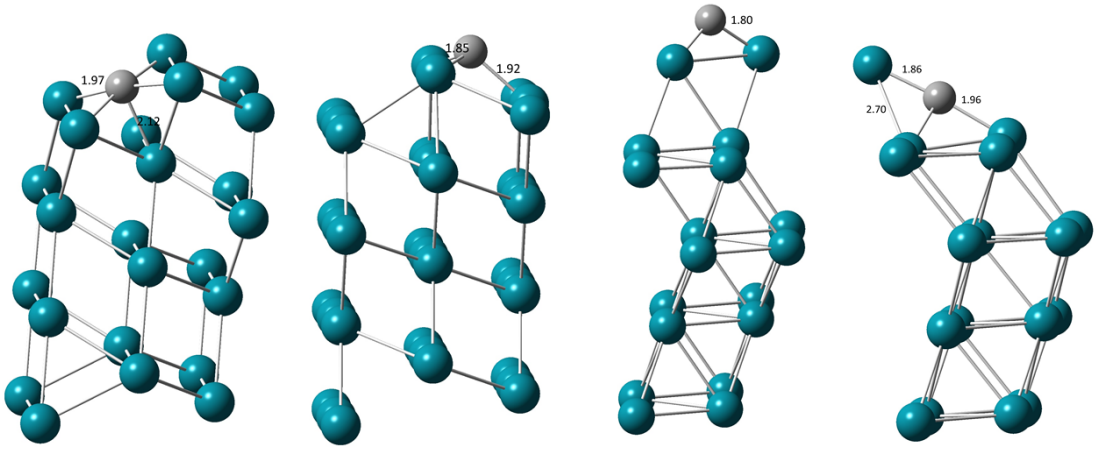


(111) (100) (110)



(211) Kink Ad-row Ad-atom

Figure S1