

Supplementary Materials

The Activation of Methane on Ru, Rh, and Pd Decorated Carbon Nanotube and Boron Nitride Nanotube: A DFT Study

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Table S1. The selected parameters of the adsorption, transition state and dissociative adsorption complex on Ru, Rh and Pd decorated carbon nanotube with M06-L/6-31G(d,p)+Stuttgart basis set. .

Parameters	Ru-C ₉₆ H ₁₆			Rh-C ₉₆ H ₁₆			Pd-C ₉₆ H ₁₆		
	AD1	TS1	DA1	AD3	TS3	DA3	AD5	TS5	DA5
Distance (Å) ^a									
M – C1	2.11	2.16	2.21	2.10	2.12	2.14	2.16	2.24	2.35
M – C2	2.24	2.19	2.26	2.15	2.27	2.15	2.17	2.54	2.43
M – H	2.11	1.63	1.64	2.06	1.57	1.55	2.07	1.55	1.56
M – C	2.49	2.12	2.05	2.48	2.09	2.04	2.44	2.07	2.04
C – H	1.11	1.58	2.77	1.11	1.71	2.43	1.11	1.87	2.27
Angle (°)									
M – H – C	95.9	82.5	47.2	98.1	78.7	56.5	95.5	73.6	61.1
Freq (cm ⁻¹) ^b		649.9i			753.6i			477.2i	

^a The M, C1 and C2 represent metal and carbon atom of the carbon nanotube. The C and H represent carbon and hydrogen atom of the methane. ^b The imaginary frequency are for the transition state structures.

Table S2. The selected parameters of the adsorption, transition state and dissociative adsorption complex on Ru, Rh and Pd decorated boron nitride nanotube with M06-L/6-31G(d,p)+Stuttgart basis set.

Parameters	Ru-B ₄₈ N ₄₈ H ₁₆			Rh-B ₄₈ N ₄₈ H ₁₆			Pd-B ₄₈ N ₄₈ H ₁₆		
	AD2	TS2	DA2	AD4	TS4	DA4	AD6	TS6	DA6
Distance (Å) ¹									
M – B	2.28	2.49	2.47	2.28	2.23	2.55	2.30	2.39	2.43
M – N	2.16	2.27	2.21	2.13	2.22	2.31	2.18	2.32	2.30
M – H	2.09	1.63	1.61	1.99	1.57	1.56	1.99	1.55	1.55
M – C	2.46	2.40	2.05	2.41	2.08	2.04	2.40	2.07	2.02
C – H	1.11	1.55	2.47	1.12	1.65	2.34	1.12	1.74	2.32
Angle (°)									
M – H – C	95.1	82.8	83.9	97.7	80.7	80.0	97.7	77.6	59.2
Freq (cm ⁻¹) ²		628.6i			600.8i			776.5i	

^a The M, B and N represent metal, boron and nitrogen atom of the boron nitride nanotube. The C and H represent carbon and hydrogen atom of the methane. ^b The imaginary frequency are for the transition state structures.

Table S3. Mulliken charge lel for the methane dissociative adsorption reaction on the Ru-, Rh- and Pd- carbon nanotube and Ru-, Rd- and Pd- boron nitride nanotube.

		Bare	AD	TS	DA
Ru-C ₉₆ H ₁₆	C ₉₆ H ₁₆		-0.40	-0.29	-0.14
	Ru	-0.44	+0.31	+0.39	+0.42
	CH ₄	+0.44	+0.09	-0.09	-0.27
Ru-B ₄₈ N ₄₈ H ₁₆	B ₄₈ N ₄₈ H ₁₆		+0.24	+0.13	+0.18
	Ru	+0.05	-0.17	-0.04	+0.11
	CH ₄	-0.05	+0.07	-0.09	-0.29
Rh-C ₉₆ H ₁₆	C ₉₆ H ₁₆		-0.33	-0.22	-0.14
	Rh	-0.32	+0.26	+0.34	+0.36
	CH ₄	+0.32	+0.07	-0.12	-0.22
Rh-B ₄₈ N ₄₈ H ₁₆	B ₄₈ N ₄₈ H ₁₆		+0.16	+0.29	+0.24
	Rh	+0.12	-0.22	-0.07	-0.06
	CH ₄	-0.12	+0.06	-0.22	-0.18
Pd-C ₉₆ H ₁₆	C ₉₆ H ₁₆		-0.23	-0.15	-0.03
	Pd	-0.22	+0.17	+0.24	+0.22
	CH ₄	+0.22	+0.06	-0.09	-0.19
Pd-B ₄₈ N ₄₈ H ₁₆	B ₄₈ N ₄₈ H ₁₆		+0.21	+0.23	+0.28
	Pd	+0.14	-0.25	-0.07	-0.08
	CH ₄	-0.14	+0.04	-0.16	-0.20

Table S4. The relative energies (kcal mol⁻¹) of the adsorption and dissociative adsorption of methane on Ru, Rh and Pd decorated carbon nanotube and boron nitride nanotube with M06-L/6-31G(d,p)+Stuttgart basis set. .

	Spin	AD	DA
Ru- C ₉₆ H ₁₆	3	-12.0	-3.6
	5	-5.4	4.9
Ru-B ₄₈ N ₄₈ H ₁₆	3	-14.8	-17.8
	5	15.8	5.6
Rh-C ₉₆ H ₁₆	2	-11.2	2.4
	4	-5.9	7.2
Rh-B ₄₈ N ₄₈ H ₁₆	2	-14.3	-4.6
	4	15.8	23.0
Pd-C ₉₆ H ₁₆	1	-0.9	24.5
	3	-10.1	15.4
	5	-11.7	12.5
Pd-B ₄₈ N ₄₈ H ₁₆	1	-13.3	2.7
	3	35.0	43.1
	5	127.9	133.8