Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

First-Principles Theory Study on Dry Reforming of Methane over Perfect and Boron Vacancies of h-BN Sheets Supported Ni Catalysts

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Table S1 Standard entropy of gas phase material at 973.15 K

Species	S°(J/mol*K)[2]
CH_4	245.61
CO_2	267.82
H_2	165.39
CO	233.63
H_2O	231.62

Table S2 Calculated energy barriers (*Ea*) and reaction energy (*ΔE*) for all the elementary reactions involved in dry reforming of methane.

		CH_4*→CH_3*+H*		CO_2*→CO*+O*	
	Catalyst	E_a(eV)	*ΔE* (eV)	E_a (eV)	*ΔE*(eV)
1	Ni_1/h-BN	0.46	0.42	2.11	1.74
2	Ni_1/h-BN-B-D	1.48	1.30	2.78	2.61
3	Ni_2/h-BN	0.11	-0.04	1.11	0.22
4	Ni_2/h-BN-B-D	0.36	0.35	1.42	0.24

Table S3 Adsorption energy of key species involved in DRM over Ni_2/h-BN, Ni_2/h-BN-B-D and Ni(111) (eV).

	Ni_2/h-BN	Ni_2/h-BN-B-D	Ni(111)[1]
CH_4	-0.58	-0.84	-0.02
CH_3	-3.74	-2.63	-1.92
CH_2	-4.29	-3.86	-4.01
CH	-5.11	-4.84	-6.43
C	-6.40	-6.02	-6.78
CH_3O	-3.95	-2.55	-2.36
CH_2O	-2.67	-1.14	-0.75
CHO	-4.05	-2.90	-2.26
CO_2	-2.05	-1.57	-0.02
CO	-3.45	-2.48	-1.92
COOH	-3.26	-2.83	-2.26
OH	-5.19	-3.82	-3.42
O	-6.33	-5.38	-5.67
H	-3.58	-2.67	-2.81
H_2O	-0.57	-1.01	-0.29

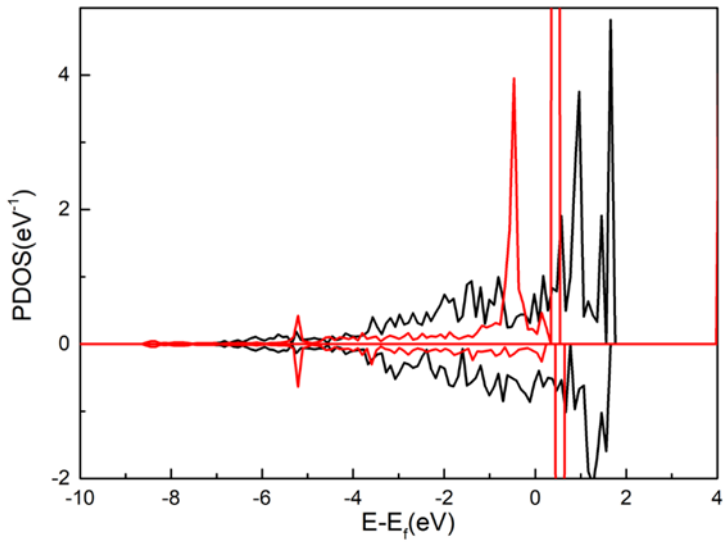


Fig.S1 Partial density of state (PDOS) of Ni_2 absorbed on perfect h-BN surface (red) and B-defect h-BN surface (black).All the Fermi levels are shifed to 0.0 eV.

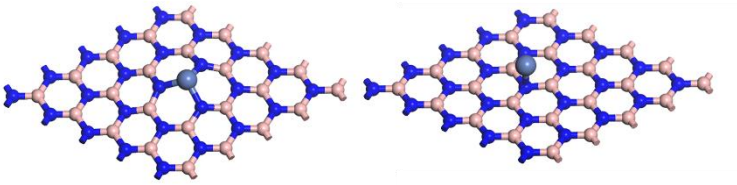


Fig. S2 Single Ni adsorption configuration on B-defected (left) and prefect (right) h-BN

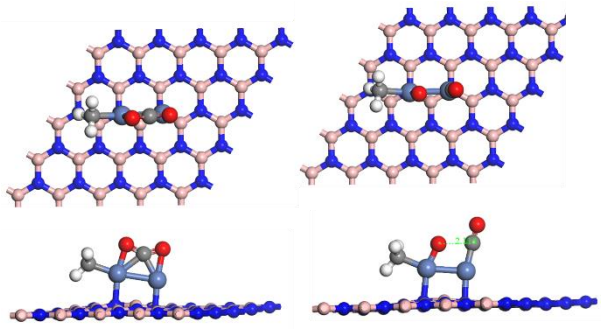


Fig. S3. IS and TS configurations of the CO_2 direct activation on Ni_2/h-BN In the presence of CH_3.

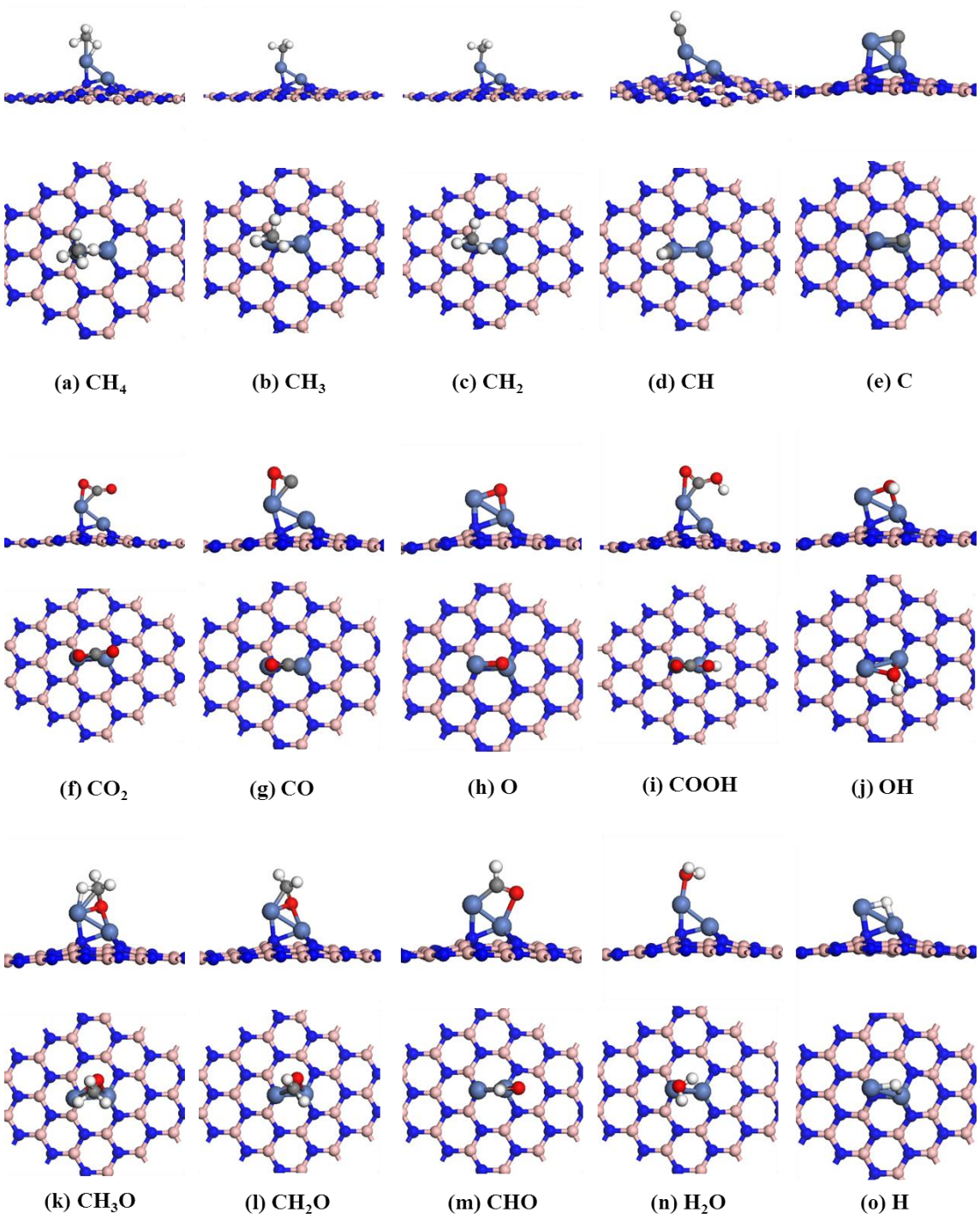


Fig. S4 Most stable adsorption structures for the intermediates on Ni_2/h-BN-B-D. The red, white and gray balls denote the O, H and C atoms, respectively.

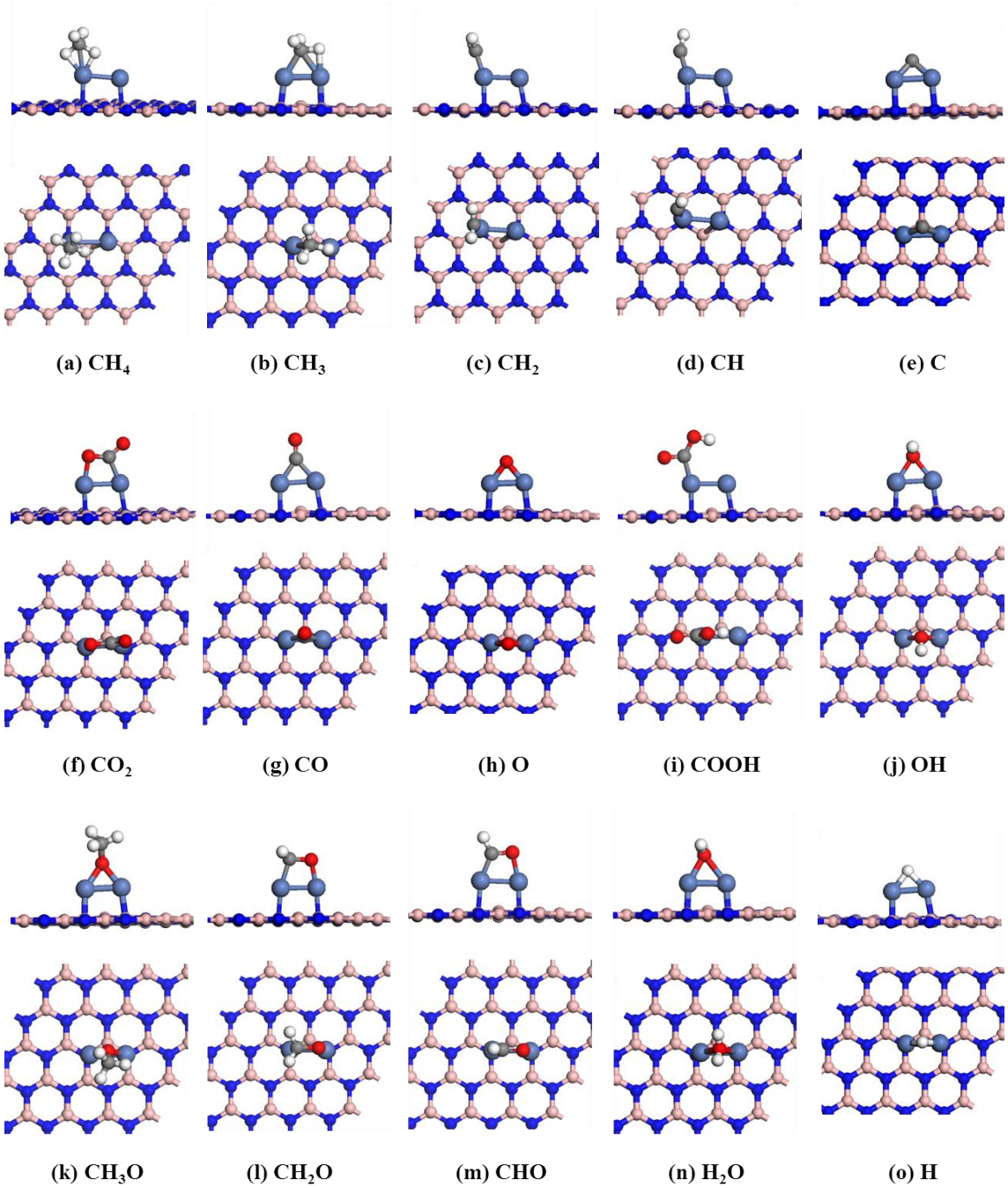


Fig. S5 Most stable adsorption structures for the intermediates on Ni_2/h-BN. The red, white and gray balls denote the O, H and C atoms, respectively.

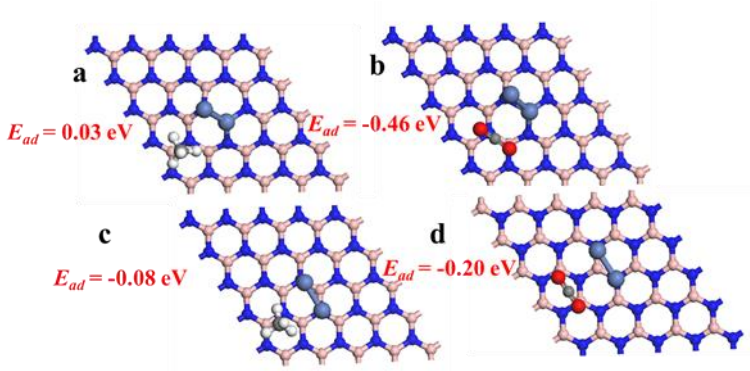
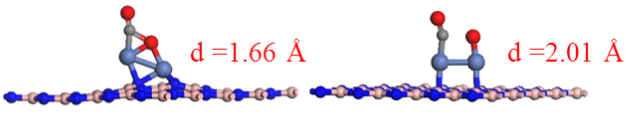
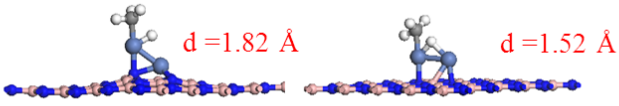


Fig.S6 Most stable adsorption structures and adsorption energy of CH_4 and CO_2 over h-BN in DRM on Ni2/h-BN-B-D(a,b) and Ni2/h-BN(c,d). The red, white and gray balls denote the O, H and C atoms, respectively.



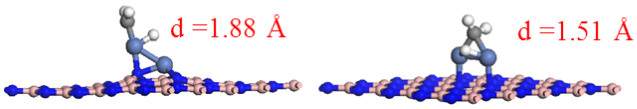
f/i = 450.354573 cm^{-1} f/i = 314.860984 cm^{-1}

CO_2 * → CO* + O*



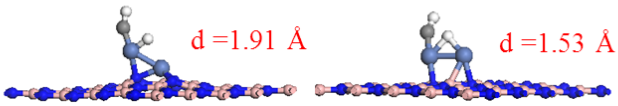
f/i = 575.995735 cm^{-1} f/i = 702.133100 cm^{-1}

CH_4 * → CH_3* + H*



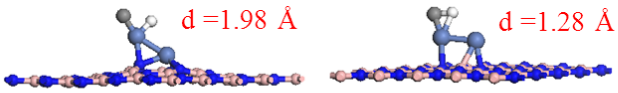
f/i = 600.371573 cm^{-1} f/i = 610.558920 cm^{-1}

CH_3 * → CH_2* + H*



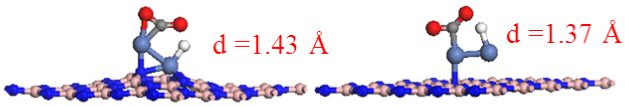
f/i = 648.528508 cm^{-1} f/i = 353.541318 cm^{-1}

CH_2 * → CH* + H*



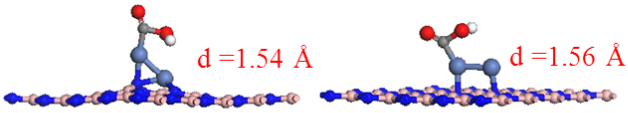
f/i = 223.124880 cm^{-1} f/i = 324.278117 cm^{-1}

CH* → C* + H*



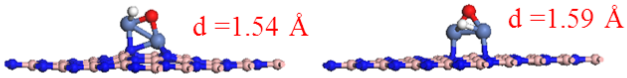
f/i = 1098.122522 cm^{-1} f/i = 1284.518997 cm^{-1}

CO_2 * + H* → COOH*



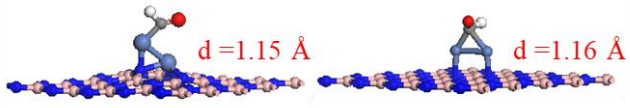
f/i = 240.446327 cm^{-1} f/i = 367.247134 cm^{-1}

COOH* → CO* + OH*



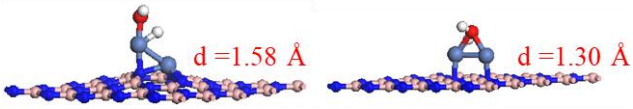
f/i = 899.667620 cm^{-1} f/i = 879.858888 cm^{-1}

OH* → O* + H*



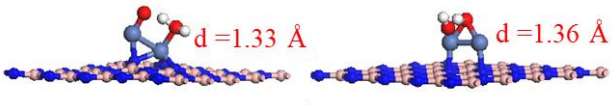
f/i = 236.129557 cm^{-1} f/i = 501.510748 cm^{-1}

CHO* → CO* + H*



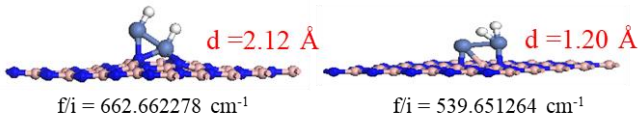
f/i = 976.994778 cm^{-1} f/i = 895.836361 cm^{-1}

H_2O* → HO* + H*



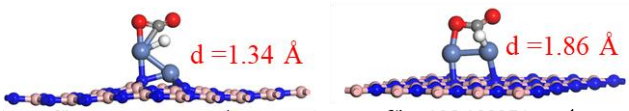
f/i = 592.502695 cm^{-1} f/i = 626.052598 cm^{-1}

2HO* → H_2O* + O*



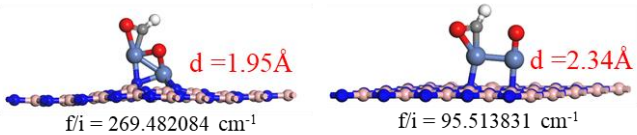
f/i = 662.662278 cm^{-1} f/i = 539.651264 cm^{-1}

2H* → H_2*



f/i = 88.119957 cm^{-1} f/i = 125.188274 cm^{-1}

CO_2* + H* → HCOO*



f/i = 269.482084 cm^{-1} f/i = 95.513831 cm^{-1}

HCOO* → HCO* + O*

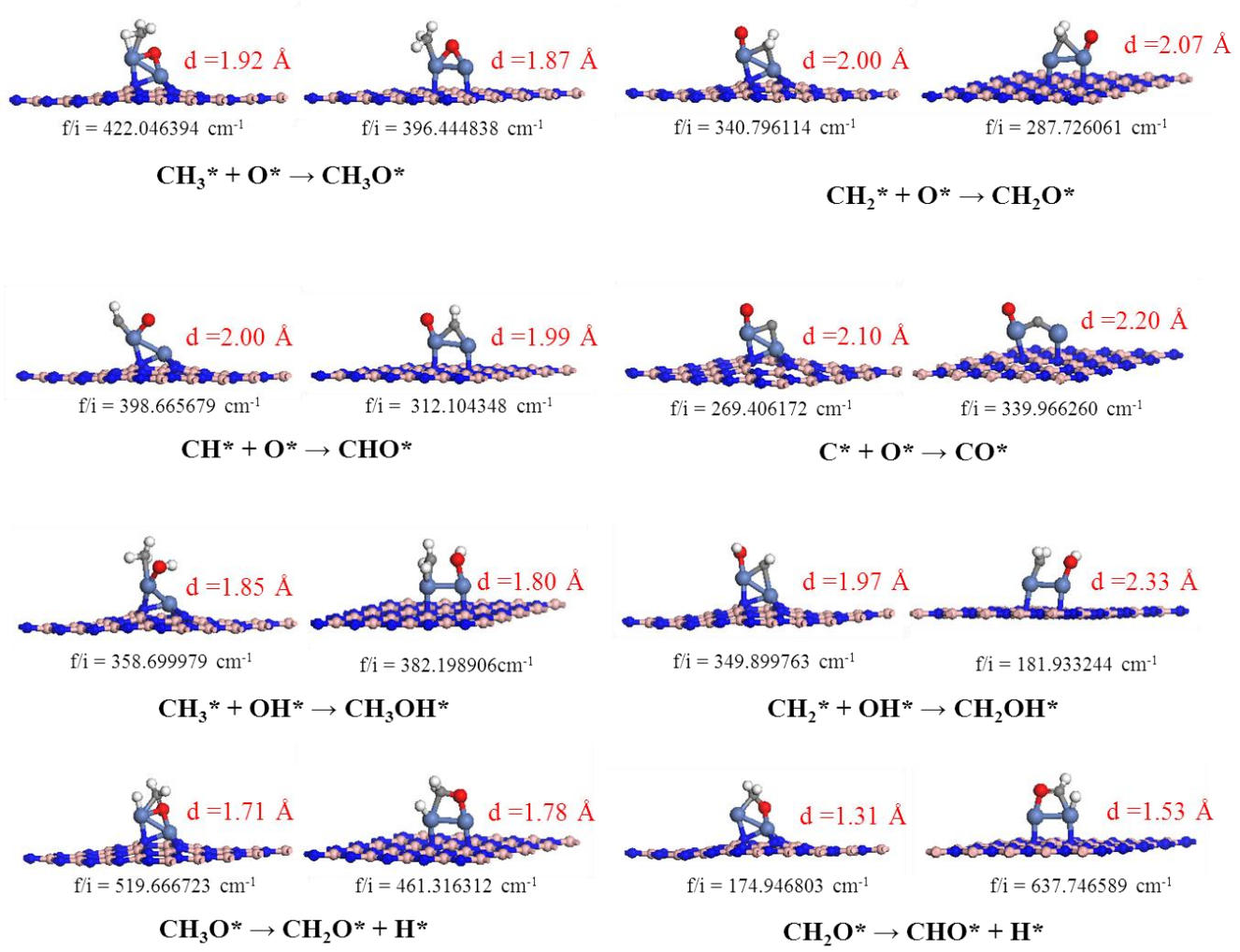


Fig.S7 TSs configuration in DRM on Ni_2/h-BN-B-D and Ni_2/h-BN. The red, white and gray balls denote the O, H and C atoms, respectively.

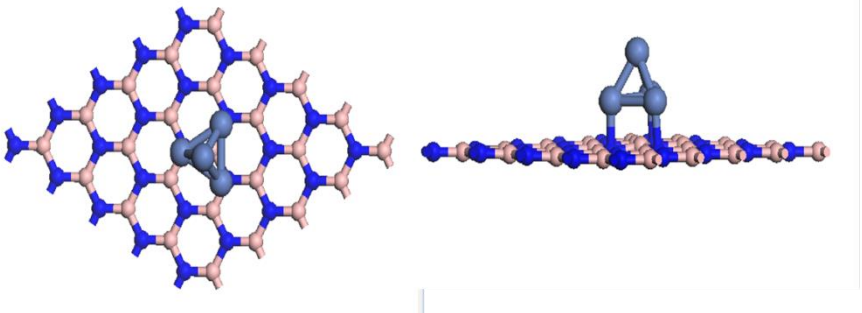


Fig.S8 Top and side view of Ni_4 adsorption configuration on prefect h-BN.

Reference

[1] W. K. Yuan, Y.A. Zhu, Catalysis Today. **2009**, *148*, 260–267.

[2] Chase, M.W., Jr., NIST-JANAF Themochemical Tables, Fourth Edition, J. Phys. Chem. Ref. Data, Monograph 9, **1998**,

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