A DFT Study of Boron Nitride-confined Nickel Single Atoms for the Oxidation of Methane to Methanol

Sanmei Wang,[a] Bo Yu,[b*] Liangbing Wang[a*]

[a] *State Key Laboratory for Powder Metallurgy, School of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, P. R. China*

[b] *Ningbo Fengcheng Advanced Energy Materials Research Institute, Fenghua District, Ningbo, Zhejiang, 315500, China*

[*]To whom correspondence should be addressed.

E-mail: yu.bo@fcnano.cn; wanglb@csu.edu.cn

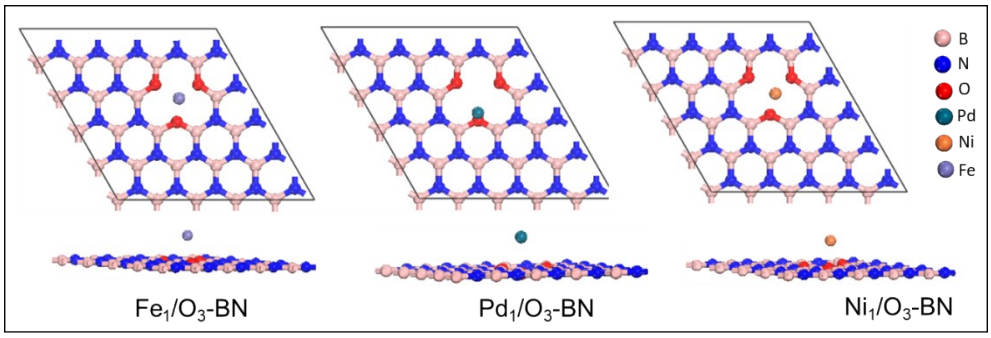

Fig. S1 Optimized structures of M_1/O_3-BN (M=Fe, Pd, Ni). The purple, orange, cyan, dark blue, bright red, and pink spheres represented Fe, Ni, Pd, N, O, and B atoms, respectively.

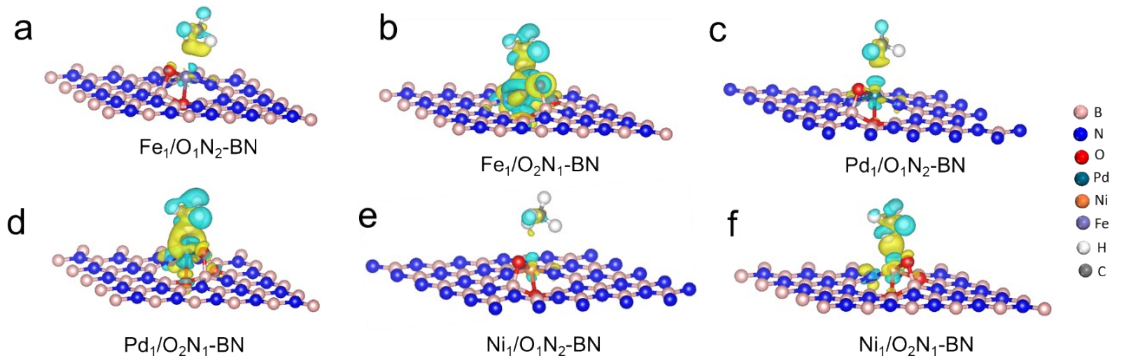

Fig. S2 Charge density difference for CH_4 molecule adsorbed on (a) Fe_1/O_1N_2-BN, (b) Fe_1/O_2N_1-BN, (c) Pd_1/O_1N_2-BN, (d) Pd_1/O_2N_1-BN, (e) Ni_1/O_1N_2-BN, and (f) Ni_1/O_2N_1-BN. The isosurface value was 0.0015 e/Å^3. The gray, white, purple, orange, cyan, dark blue, bright red, and pink spheres represented C, H, Fe, Ni, Pd, N, O, and B atoms, respectively.

Table S1 The charge-transfer values from CH_4 to the catalyst. The integrated crystal orbital Hamilton population (ICOHP) between the metal atoms and the C atom of adsorbed CH_4.

	charge-transfer values (e)	ICOHP (eV)
Fe_1/O_1N_2-BN	0.01	-2.46
Fe_1/O_2N_1-BN	0.03	-2.71
Pd_1/O_1N_2-BN	0.01	-3.03
Pd_1/O_2N_1-BN	0.11	-3.13
Ni_1/O_1N_2-BN	0.003	-2.50
Ni_1/O_2N_1-BN	0.03	-2.68

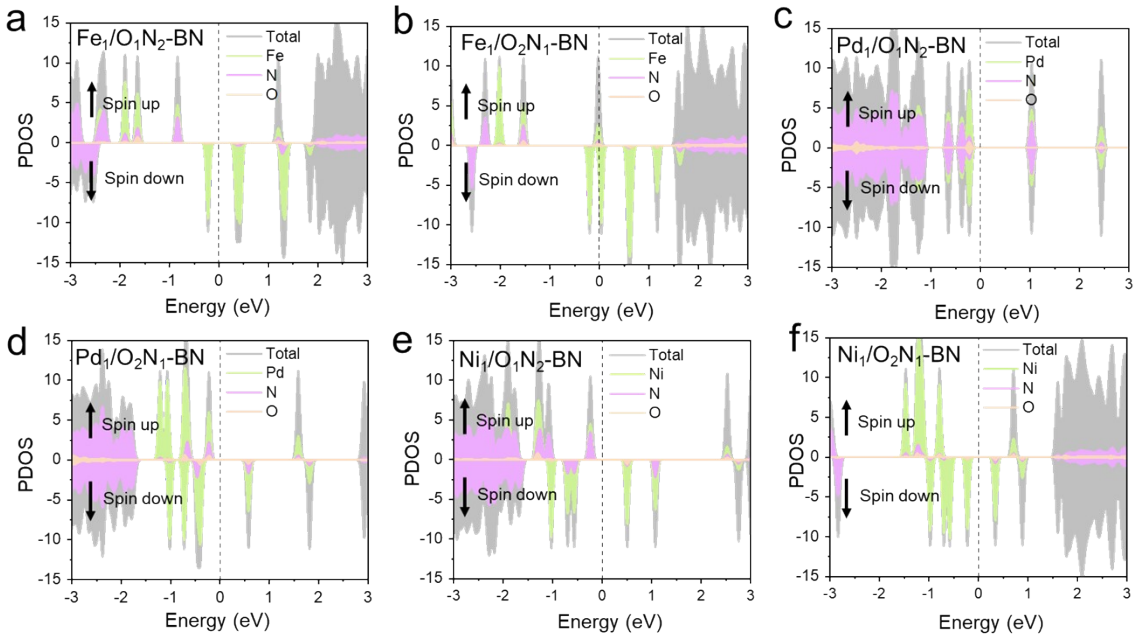

Fig. S3 Density of states (DOS) of (a) Fe_1/O_1N_2-BN, (b) Fe_1/O_2N_1-BN, (c) Pd_1/O_1N_2-BN, (d) Pd_1/O_2N_1-BN, (e) Ni_1/O_1N_2-BN, and (f) Ni_1/O_2N_1-BN catalysts. The dotted black lines represented the Fermi energy level.

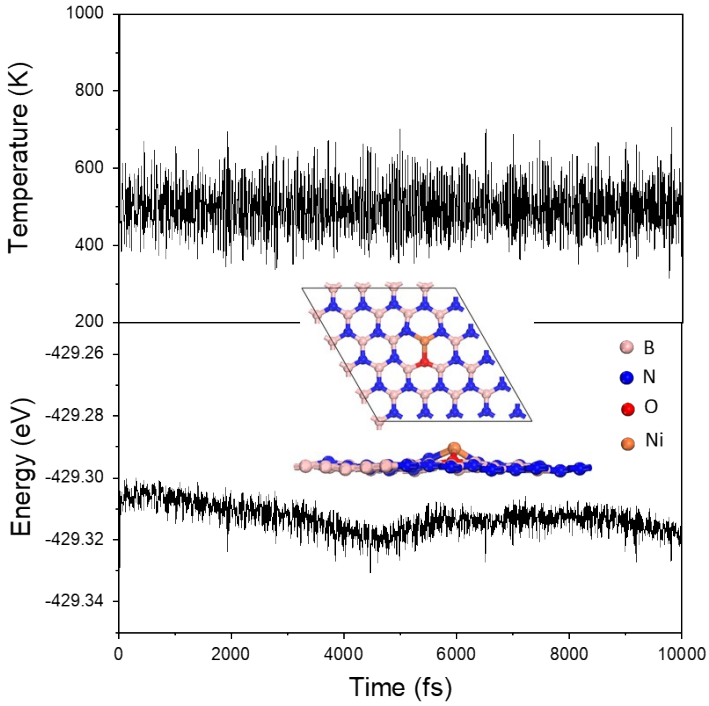

Fig. S4 Variations of energy and temperature against the time for the AIMD simulations of Ni_1/O_1N_2-BN. Insert pictures were top and side views of Ni_1/O_1N_2-BN after running 10 ps with a time-step of 1 fs at 500 K.