

Direct conversion of methane to methanol on boron nitride-supported copper single atoms

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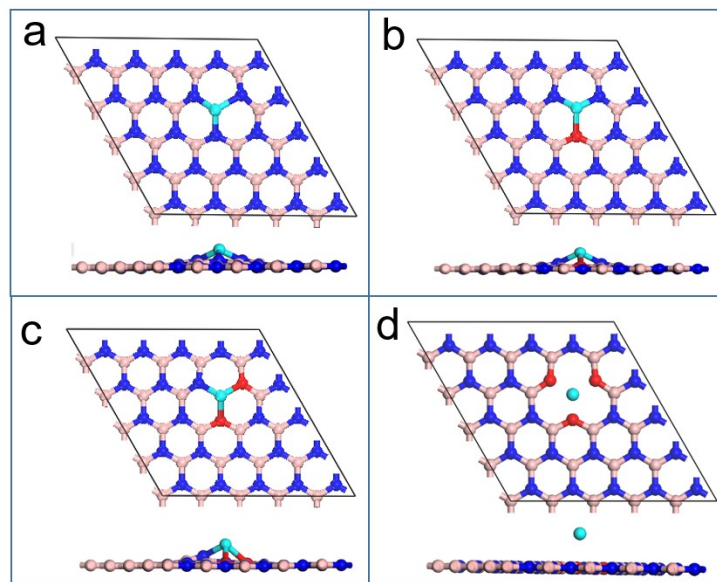


Fig. S1 Optimized structures for Cu-embedded into (a) N_3 -BN substrate (Cu_1/N_3 -BN), (b) O_1N_2 -BN substrate (Cu_1/O_1N_2 -BN), (c) O_2N_1 -BN substrate (Cu_1/O_2N_1 -BN), and (d) O_3 -BN substrate (Cu_1/O_3 -BN). The light blue, dark blue, bright red, and pink spheres represented Cu, N, O, and B atoms, respectively.

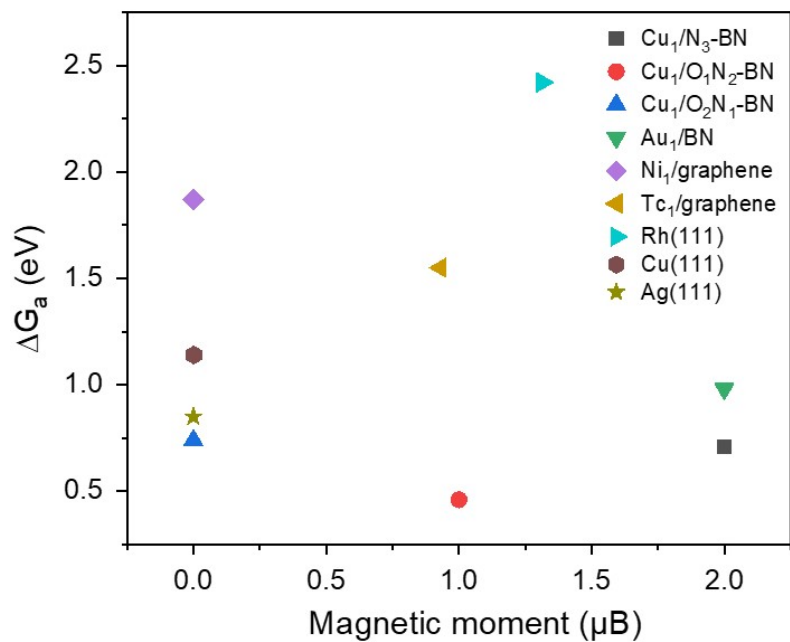


Fig. S2 The relationship between the magnetic moment and the free energy barriers of CH_4 activation was not a volcano curve.

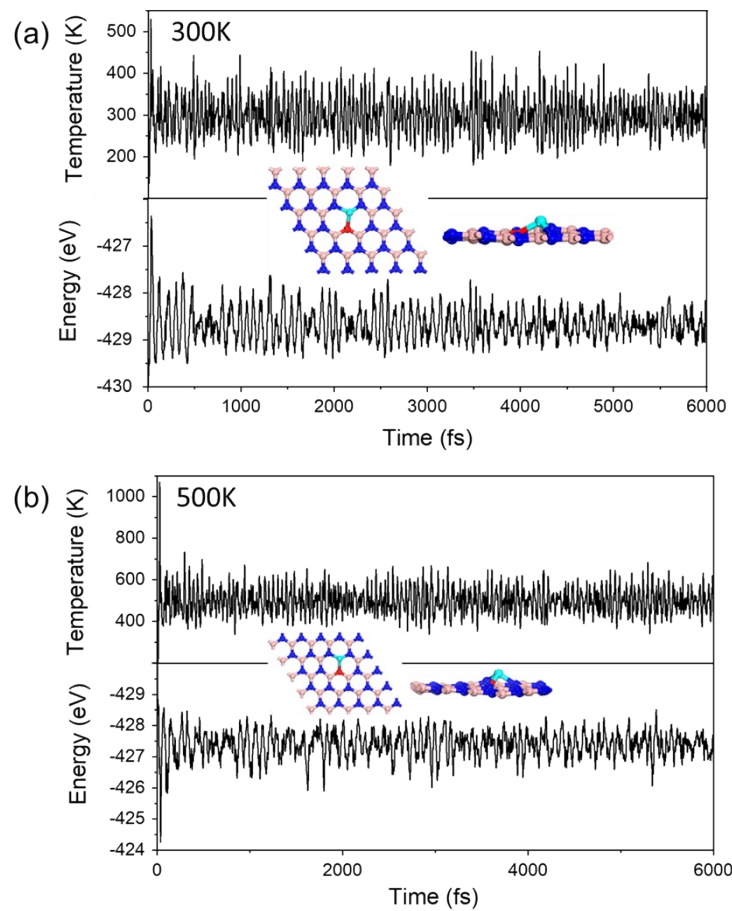
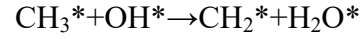
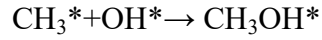


Fig. S3 The calculated ab initio MD to investigate the stability of $\text{Cu}_1/\text{O}_1\text{N}_2\text{-BN}$. Variations of temperature and energy at (a) 300K and (b) 500K, insert are top and side views of the snapshot of atomic configuration. Each simulation lasts 6 ps, and the time-step was set as 1 fs.

The calculation for the production rate of CH₃OH and CH₂

According to the reaction for generating CH₃OH and CH₂,



the $r_{\text{CH}_3\text{OH}}$ and r_{CH_2} were calculated according to Eq. S2 and S3, respectively.

$$r_{\text{CH}_3\text{OH}} = k_{\text{CH}_3\text{OH}} C_{\text{CH}_3^*} C_{\text{OH}^*} \quad (\text{S1})$$

$$r_{\text{CH}_2} = k_{\text{CH}_2} C_{\text{CH}_3^*} C_{\text{OH}^*} \quad (\text{S2})$$

where $C_{\text{CH}_3^*}$ and C_{OH^*} denoted the concentration of intermediates CH₃* and OH*, respectively. The ratio of CH₃OH production rate to CH₂ production rate was

$\frac{r_{\text{CH}_3\text{OH}}}{r_{\text{CH}_2}} = \frac{k_{\text{CH}_3\text{OH}}}{k_{\text{CH}_2}}$. The production rate of CH₃OH was determined to be 1.81×10^6 times than

that of CH₂ species at room temperature, indicating the negligible production of CH₂ species relative to CH₃OH.

Stability of Cu₁/O₁N₂-BN catalyst

In addition, we also calculated the formation energy of Cu atoms embedded in O₁N₂-BN substrate to further determine the stability of Cu₁/O₁N₂-BN. The formation energy was calculated by equation (1):

$$E_f = E_{\text{Cu}_1/\text{O}_1\text{N}_2\text{-BN}} - E_{\text{O}_1\text{N}_2\text{-BN}} - E_{\text{Cu}}$$

Where $E_{\text{Cu}_1/\text{O}_1\text{N}_2\text{-BN}}$, $E_{\text{O}_1\text{N}_2\text{-BN}}$, and E_{Cu} were the energies of Cu₁/O₁N₂-BN, O₁N₂-BN substrate, Cu single atoms in its bulk form, respectively. The formation energy was determined to be -0.74 eV, indicating that the structure for Cu atoms embedded in O₁N₂-BN substrate via two O-Cu and one N-Cu coordination were stable.

Table S1 DFT-calculated activation energies of CH₄ and adsorption free energy of *O atoms. Structures taken from Ref.^{S1} and Ref.^{S2} was indicated by ‡ and *, respectively, and we recalculated the activation energies of CH₄ for these structures. All values were in eV.

Catalyst	Catalyst Type	$\Delta G_{\text{ads}}(*\text{O})$	$\Delta G_{\text{a}}(\text{CH}_4)$
Cu	O ₂ N ₁ -BN	-0.80	0.74
Cu	O ₁ N ₂ -BN	-0.15	0.46
Cu	BN	0.13	0.71
Au [‡]	BN	-0.90	0.98
Ni [*]	graphene	-2.01	1.87
Tc [‡]	graphene	-2.15	1.55
Rh [‡]	metal-111	-2.77	2.42
Cu [‡]	metal-111	-1.61	1.14
Ag [‡]	metal-111	-0.56	0.85

Synthesis of Cu₁/O₁N₂-BN catalyst

A feasible synthesis method of Cu₁/O₁N₂-BN catalyst was proposed by calculation, as illustrated in Fig. S4†. Cu₁/O₁N₂-BN catalyst can be prepared by Cu-modified h-BN where a Cu atom bonded with two unsaturated nitrogen (N) atoms and two boron (B) atoms (named as Cu₁/BN) at the presence of H₂O₂. A H₂O₂ was adsorbed on Cu₁/BN with G_{ads} of 0.21 eV. And then the H₂O₂ was decomposed on Cu₁/BN through the breakage of O-O bonds or O-H bonds.

The ΔG_a for the breakage of the O-O bond to form two OH species ($*\text{H}_2\text{O}_2 \rightarrow 2*\text{OH}$) was calculated to be 0.44 eV, obviously lower than that of the O-H bond breakage to form OOH species and H species (1.08 eV, $*\text{H}_2\text{O}_2 \rightarrow *\text{OOH} + *\text{H}$). Thus, the breakage of O-O bonds were more dynamically favorable than the O-H bond breakage on Cu₁/BN. These two $*\text{OH}$ species further combined with each other to form a H₂O molecule and a lattice O with ΔG_a of 0.79 eV. After the adsorbed H₂O released from the surface of Cu₁/O₁N₂-BN, Cu₁/O₁N₂-BN catalyst was fabricated.

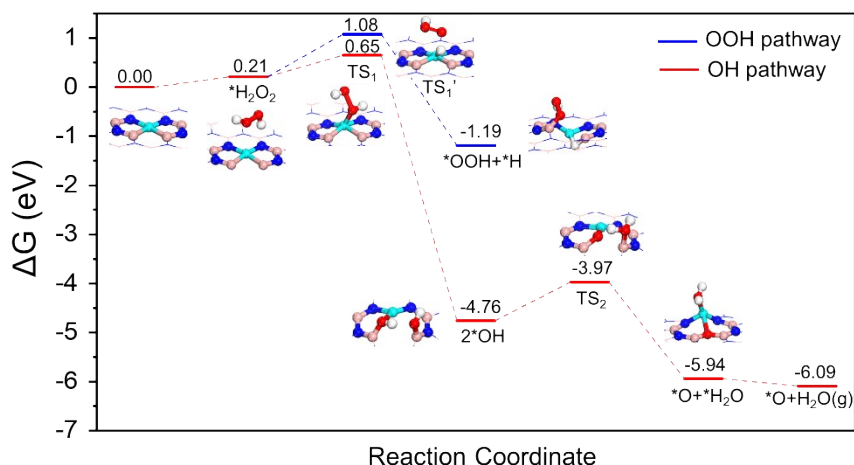


Fig. S4 Free energy diagrams for the decomposition of H₂O₂ over Cu₁/BN. TS represented the transition states. The gray, white, light blue, dark blue, bright red, and pink spheres represented C, H, Cu, N, O, and B atoms, respectively.

Reference

S1 A. A. Latimer, A. Kakekhani, A. R. Kulkarni and J. K. Nørskov, *ACS Catal.*, 2018, 8, 6894–6907.

S2 S. M. Wang, Y. Xin, W. H. Zhang and L.B. Wang, *Catal. Lett.*, DOI:10.1007/s10562-021-03742-1.