

Understanding the Water Molecule Effect in Metal-Free B-Based Electrocatalyst for Electrochemical CO₂ Reduction

*Yuxiao Meng^b, Zhangmeng Xu^a, Zhangfeng Shen^a, Qineng Xia^a, Yongyong Cao^{*a},
Yangang Wang^{*a}, Xi Li^{*a}*

- a. College of Biological, Chemical Science and Engineering Jiaxing University,
Jiaxing, Zhejiang, 314001 (P. R. China).*
- b. Institute of Industrial Catalysis, College of Chemical Engineering, State Key
Laboratory Breeding Base of Green-Chemical Synthesis Technology, Zhejiang
University of Technology, Hangzhou 310032 (P. R. China)*

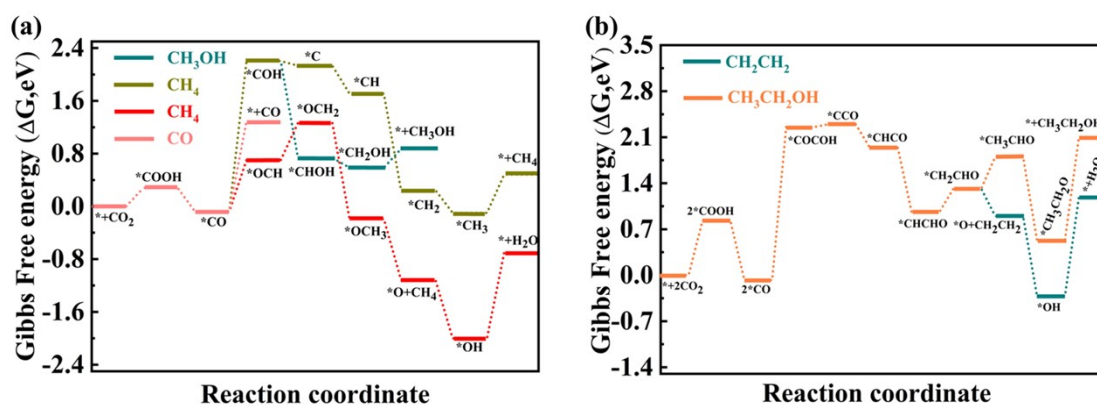


Fig. S1 (a) The free energy diagram of the CO₂ reaction to CH₃OH, CH₄ and CO on the B@Bi surface by RPBE functional. (b) The free energy diagram of the CO₂ reaction to CH₂CH₂ and CH₃CH₂OH on the B₂@Bi surface by RPBE functional.

All intermediates of the CO₂RR pathways on B@Bi and B₂@Bi catalysts were optimized using revised Perdew-Burke-Ernzerh (RPBE) functional. As shown in Fig. S1a and b, the first proton-electron transfer step to *COOH formation with RPBE is energetically uphill by 0.28 eV on B@Bi, respectively. The *CO intermediate would be further hydrogenated to form *OCH species or *COH intermediate, respectively. The energy barriers are 0.78 eV and 2.28 eV, respectively. Consequently, the *OCH formation is more profitable than *COH formation. Subsequently, the further hydrogenation of *OCH to form *OCH₂, *OCH₃ and *O+CH₄ products. The reaction path for CH₄ formation is more favorable than CO and CH₃OH on B@Bi catalyst and the rate-determining step is the *OCH formation with an energy barrier of 0.78 eV. Similar to B@Bi catalyst, the adsorbed two CO₂ captures H proton and generates the intermediate *COOH with energetically uphill of 0.83 eV. The *COOH protonation process occurs to form the *CO species by -0.91 eV. The *COCO product can be formed following *CO protonation and C-C coupling with a barrier of 2.33 eV. While the adsorbed CO₂ is still more likely to generate CH₂CH₂ on the B₂@Bi catalyst due to the steric hindrance make the *CH₂CH₂O species formation energetically downhill by -0.42 eV. The generation of *COCO is considered as the rate-determining step with a free energy value of 2.33 eV. The selectivity of the two pathways on B@Bi and

B₂@Bi have been estimated by calculating the limit-potential. The results indicates that the trends of selectivity for products unaltered. The U_L value for the CH₄ formation by *OCH hydrogenation is -0.78 V, while the value for the CH₄ and CH₃OH products following *COH hydrogenation is -2.28 V using RPBE functional. For B₂@Bi catalyst, the U_L value for the CH₂CH₂ and CH₃CH₂OH products is -2.33 V. As a result, the selective evaluation for CH₄ and CH₂CH₂ products by RPBE functional are consistent with the PBE functional.

Table S1. The free energy difference of the elementary reaction by PBE and RPBE functional on B@Bi catalyst.

Elementary steps	PBE/ ΔG (eV)	RPBE/ ΔG (eV)
*+CO ₂ +H ⁺ +e ⁻ → *COOH	-0.46	0.28
*COOH+H ⁺ +e ⁻ → *CO+H ₂ O	-0.09	-0.36
*CO+H ⁺ +e ⁻ → *COH	2.23	2.28
*COH+H ⁺ +e ⁻ → *C+H ₂ O	0.16	-0.07
*C+H ⁺ +e ⁻ → *CH	-0.36	-0.42
*CH+H ⁺ +e ⁻ → *CH ₂	-1.39	-1.47
*CH ₂ +H ⁺ +e ⁻ → *CH ₃	-0.25	-0.34
*CH ₃ +H ⁺ +e ⁻ → *CH ₄	0.67	0.58
*COH+H ⁺ +e ⁻ → *CHOH	-1.39	-1.46
*CHOH+H ⁺ +e ⁻ → *CH ₂ OH	-0.04	-0.15
*CH ₂ OH+H ⁺ +e ⁻ → *CH ₃ OH	0.28	0.29
*CO+H ⁺ +e ⁻ → *OCH	0.82	0.78
*CHO+H ⁺ +e ⁻ → *OCH ₂	0.61	0.56
*CH ₂ O+H ⁺ +e ⁻ → *OCH ₃	-1.40	-1.46
*CH ₃ O+H ⁺ +e ⁻ → *OCH ₄	-0.85	-0.93
*O+H ⁺ +e ⁻ → *OH	-0.80	-0.88

Table S2. The free energy difference of the elementary reaction by PBE and RPBE functional on B₂@Bi catalyst.

Elementary steps	PBE/ ΔG (eV)	RPBE/ ΔG (eV)
*+2CO ₂ +2H ⁺ +2e ⁻ → 2*COOH	-0.61	0.83
2*COOH+2H ⁺ +2e ⁻ → 2*CO+2H ₂ O	-0.45	-0.91
2*CO+H ⁺ +e ⁻ → *COCO	2.21	2.33
*COCO+H ⁺ +e ⁻ → *COC+H ₂ O	0.12	0.04
*COC+H ⁺ +e ⁻ → *CHCO	-1.46	-0.35
*CHCO+H ⁺ +e ⁻ → *CHCHO	-0.19	-0.98
*CHCHO+H ⁺ +e ⁻ → *CH ₂ CHO	0.92	0.35
*CH ₂ CHO+H ⁺ +e ⁻ → *CH ₂ CH ₂ O	-0.14	-0.42
*O+H ⁺ +e ⁻ → *OH	-0.91	-1.22
*CH ₂ CHO+H ⁺ +e ⁻ → *CH ₃ CHO	0.58	0.49
CH ₃ CHO+H ⁺ +e ⁻ → CH ₃ CH ₂ O	-1.13	-1.28
*CH ₃ CH ₂ O+H ⁺ +e ⁻ → *CH ₃ CH ₂ OH	1.69	1.56

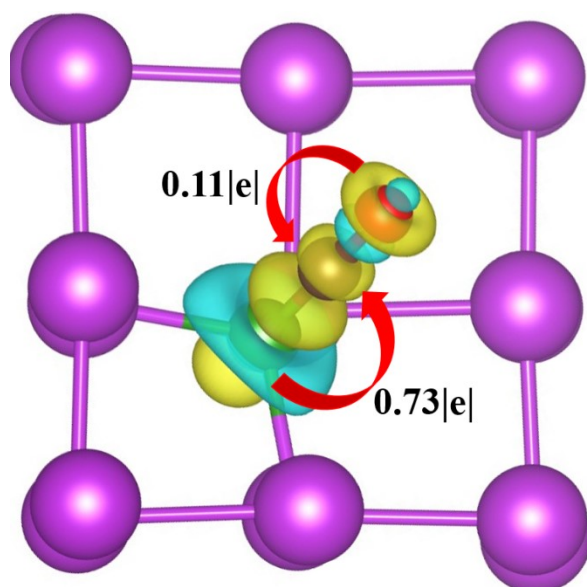


Fig. S2 Local diagram Bader charge and charge density different (CDD) of the key intermediate *CO. The accumulation and depletion are shown in yellow and blue, respectively. The isosurface value is taken as $0.005 \text{ e}/\text{\AA}^{-3}$.

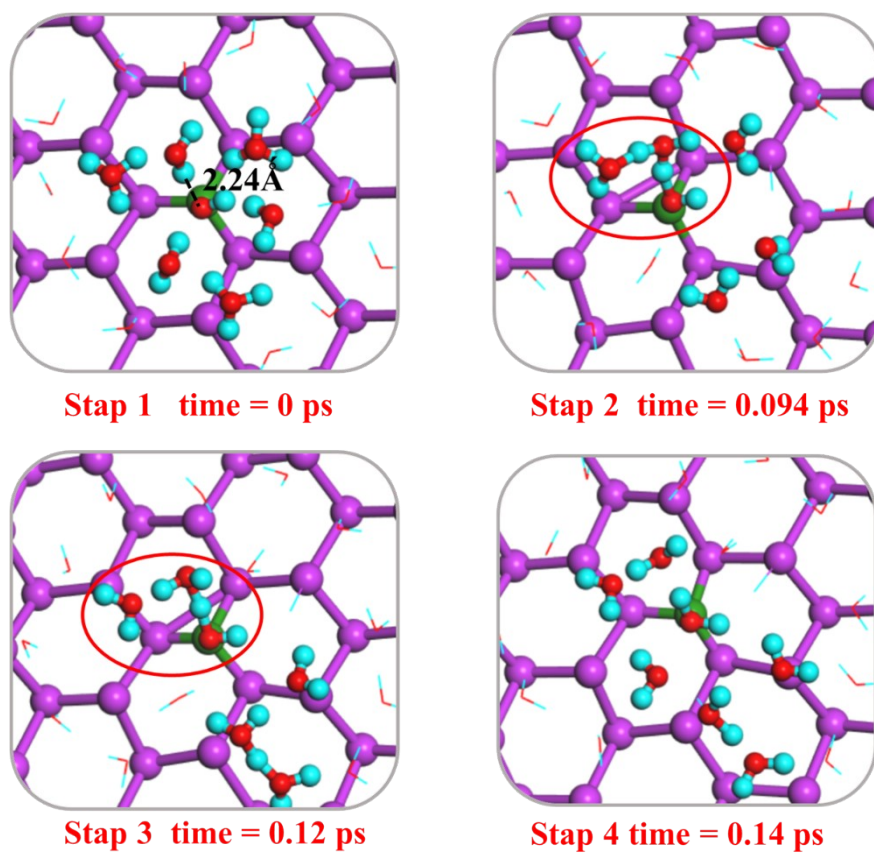
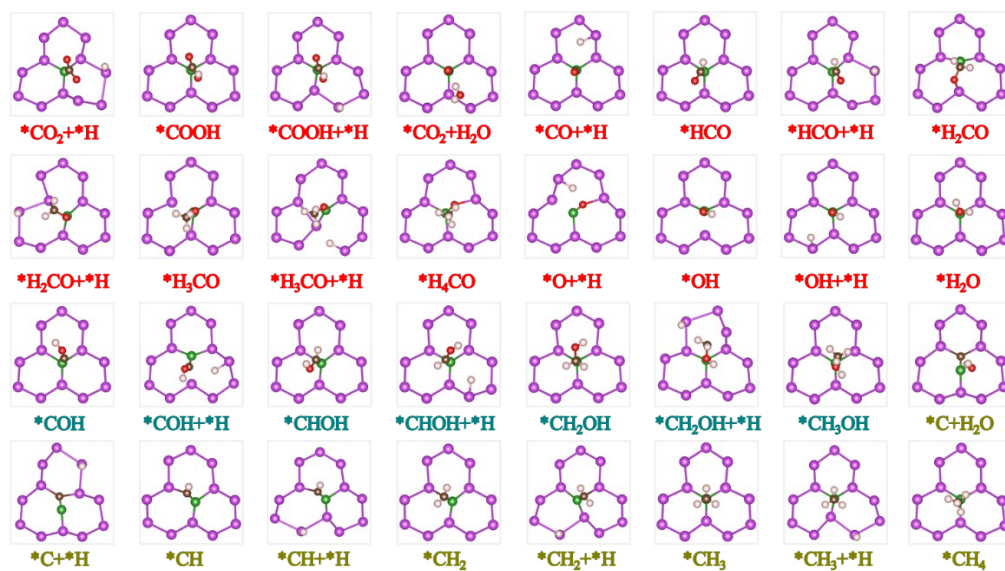


Fig. S3 *Ab-initio* molecular dynamics calculation for the conversion of *OH to H₂O molecules under acidic condition on B@Bi catalyst. The color codes are: Bi, purple; B, green; O, red; H, blue.

(a)



(b)

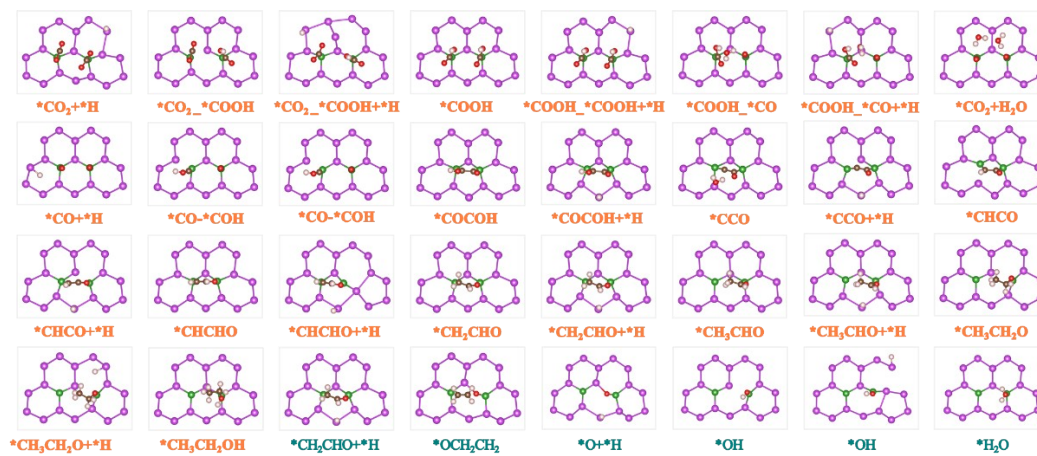


Fig. S4 The optimized initial and final structure for the CO₂ reduction on B@Bi (a) and B₂@Bi (b) catalyst.

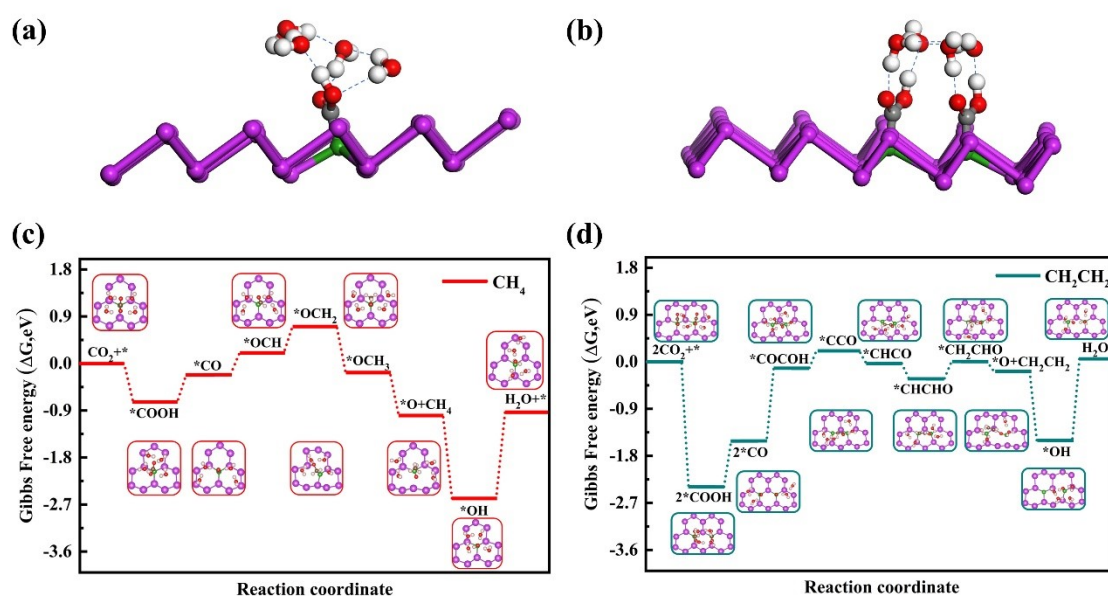


Fig. S5 (a)-(b) The intermediate $^*\text{COOH}$ adsorbed on B@Bi and $\text{B}_2\text{@Bi}$ catalysts in 4 H_2O environments. The blue dotted line represents the hydrogen bond. Color codes: Bi, purple; B, green; C, brown; O, red; H, white. The free energy distribution of the CO_2RR primitive steps of (c) B@Bi and (d) $\text{B}_2\text{@Bi}$ in the water environment.

Two optimal reaction paths on B@Bi (CH_4 path) and $\text{B}_2\text{@Bi}$ (CH_2CH_2 path) are further selected for exploring 4 H_2O molecule environments to investigate the influence of H_2O molecules on the CO_2RR mechanism (Fig. S5 c and d). The free energy barrier of CO_2RR for both B@Bi and $\text{B}_2\text{@Bi}$ decreases under the influence of H_2O molecules. On the other hand, the rate-limiting step of CO_2RR on the B@Bi is changed from the formation of the $^*\text{OCH}$ (in the gas phase) to the $^*\text{CO}$ (in the 4 H_2O environments). At a zero electrode potential ($U = 0 \text{ V}$), the polar intermediate $^*\text{COOH}$ adsorbed on B atoms can form hydrogen bonds with 4 H_2O molecules in Fig. S5 a and b, resulting in a low hydrogenation barrier. The protonation step of $^*\text{COOH}$ from the intermediate $^*\text{CO}$ requires energy barriers of 0.53 eV and 0.88 eV on B@Bi and $\text{B}_2\text{@Bi}$, respectively. Therefore, in the CO_2RR , the effect of hydrogen bonding on the stability of different polar intermediates cannot be ignored. According to the ΔG values of 1.40

eV for the *COCOH formation, the C–C coupling is considered significantly favorable to occur in *COCOH on B₂@Bi due to the involvement of H₂O molecules. In the next hydrogenation step, *COCOH is further protonated to *CCO, *CHCO, *CHCHO, *CH₂CHO, and *O+CH₂CH₂ (gas), with ΔG values of 0.33 eV, –0.24 eV, –0.30 eV, 0.33 eV and –0.19 eV, respectively. In addition, the overpotentials of the two CO₂RR mechanisms have been calculated. The B@Bi exhibited low overpotentials of 0.28 V for CH₄ and the overpotential of CH₂CH₂ formation on B₂@Bi is 1.04 V. As a result, hydrogen bond interaction between the intermediates and water molecules promotes CO₂RR protonation.

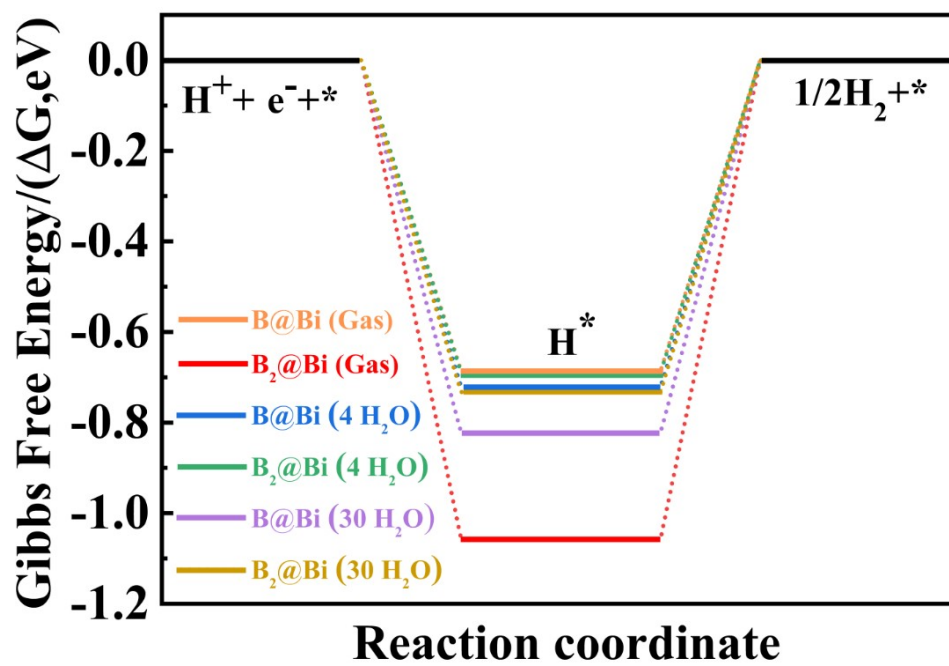


Fig. S6 Free energy diagrams of HER on B@Bi and B₂@Bi in the gas phase, 4 H₂O and 30 H₂O environment.

Table.S3 The total energy, the zero-point correction energy (ZPE), and entropy (TS, T=298.15k) of the adsorbed species on B@Bi in the gas phase.

Species	E (eV)	ZPE (eV)	TS (eV)
*COOH	-222.13	0.64	0.19
*CO	-211.65	0.24	0.10
*OCH	-214.49	0.48	0.15
*OCH ₂	-217.69	0.81	0.10
*OCH ₃	-222.85	1.13	0.15
*O+CH ₄	-227.30	1.32	0.22
*OH	-206.29	0.09	0.21
*COH	-213.05	0.44	0.13
*CHOH	-218.28	0.83	0.13
*CH ₂ OH	-222.02	1.11	0.17
*C	-202.39	0.11	0.03
*CH	-206.44	0.37	0.05
*CH ₂	-211.60	0.69	0.06
*CH ₃	-215.58	0.99	0.09

Table.S4 The total energy, the zero-point correction energy (ZPE), and entropy (TS, T=298.15k) of the adsorbed species on B₂@Bi in the gas phase.

Species	E (eV)	ZPE (eV)	TS (eV)
2*CO	-228.96	0.47	0.20
*COCOH	-230.53	0.79	0.18
*CCO	-234.02	0.99	0.24
*CHCO	-224.97	0.65	0.13
*CHCHO	-228.96	0.99	0.10
*CH ₂ CHO	-231.74	1.25	0.13
*CH ₃ CHO	-234.82	1.54	0.23
*CH ₃ CH ₂ O	-239.79	1.89	0.18
*O+CH ₂ CH ₂	-235.52	1.48	0.18
*OH	-206.86	0.39	0.07

Table.S5 The total energy, the zero-point correction energy (ZPE), and entropy (TS, T=298.15k) of the adsorbed species on B@Bi in 4 H₂O environmen.

Species	E (eV)	ZPE (eV)	TS (eV)
*COOH	-280.96	0.64	0.14
*CO	-269.82	0.23	0.09
*OCH	-273.16	0.52	0.09
*OCH ₂	-276.39	0.82	0.09
*OCH ₃	-281.01	1.14	0.14
*O+ CH ₄	-285.40	1.32	0.24
*OH	-265.56	0.39	0.04

Table.S6 The total energy, the zero-point correction energy (ZPE), and entropy (TS, T=298.15k) of the adsorbed species on B₂@Bi in 4 H₂O environmen.

Species	E (eV)	ZPE (eV)	TS (eV)
2*CO	-287.18	0.47	0.19
*COCOH	-289.58	0.79	0.14
*CCO	-292.83	1.06	0.36
*CHCO	-282.61	0.68	0.09
*CHCHO	-286.67	0.10	0.10
*CH ₂ CHO	-290.02	1.26	0.14
*O+CH ₂ CH ₂	-293.84	1.49	0.23
*OH	-265.59	0.38	0.05

Table.S7 The total energy, the zero-point correction energy (ZPE), and entropy (TS, T=298.15k) of the adsorbed species on B@Bi in 30 H₂O environmen.

Species	E (eV)	ZPE (eV)	TS (eV)
*COOH	-663.35	0.63	0.13
*CO	-652.36	0.23	0.10
*OCH	-655.75	0.51	0.10
*OCH ₂	-659.00	0.82	0.09
*OCH ₃	-663.63	1.15	0.12
*O+ CH ₄	-666.83	1.32	0.24
*OH	-647.37	0.40	0.05

Table.S6 The total energy, the zero-point correction energy (ZPE), and entropy (TS, T=298.15k) of the adsorbed species on B₂@Bi in 30 H₂O environment.

Species	E (eV)	ZPE (eV)	TS (eV)
2*CO	-669.41	0.46	0.23
*COCOH	-671.98	0.79	0.15
*CCO	-675.36	1.04	0.19
*CHCO	-664.76	0.66	0.10
*CHCHO	-668.95	0.98	0.11
*CH ₂ CHO	-672.37	1.25	0.14
*O+CH ₂ CH ₂	-676.06	1.49	0.24
*OH	-648.34	0.38	0.05