Supporting information for 'Computational study of the reaction mechanism of photo-catalytic reduction of CO₂ on anatase(101)

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S1. The effect of slab thickness on reaction energy and adsorption energy

Fig. S1 shows the dependence of reaction energy (eV) on slab thickness (2 to 6 layers), using

$CO_2 + 2H \rightarrow HCOOH$

as an example. The reaction energy is converged at 5-layer, where the reaction energy difference between 5-layer and 6-layer is 0.05 eV.



Fig. S1 Dependence of reaction energy (eV) on slab thickness.

Table 2 shows the adsorption energies of CO₂, HCOOH and H atom on the slabs with different thicknesses. The adsorption energy computed with PBE changes negligibly for CO₂ and HCOOH (less than 0.1 eV), but for H atom the difference between 2 and 5 layers is 0.3 eV, and considered converged at 4-layer. All adsorption energies of H atom computed with PBE are close to literature values, which are in between -2.01 eV¹ to -2.31 eV,² depending on the surface coverage and computational details apart from functional employed.

The adsorption energy for CO₂, HCOOH and H atom are also computed with PBE+U,³ with U = 4.0 eV.⁴ The difference between PBE with and without U for CO₂ and HCOOH are considerably small (0.07 eV and 0.12 eV respectively). For H atom, the difference (0.2 eV) is similar to those observed in the literatures,¹ but the value for

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+U computation is ~0.3 eV larger than some literature values (~ -2.30 eV).^{1,2}

 No. of layers	E_{Ad} of CO ₂ / eV	E_{Ad} of HCOOH / eV	E_{Ad} of H / eV	
 2	-0.14	-0.41	-2.10	-
3	-0.14	-0.45	-2.27	
4	-0.14	-0.44	-2.35	
5	-0.14 (-0.21)	-0.46 (-0.58)	-2.40 (-2.61)	
6	-0.15	-0.48	-2.43	

Table S2 Adsorption energies (eV) of CO₂, HCOOH and H on anatase(101) slab with 2 to 6 layers, computed with PBE. Numbers in bracket are computed with in PBE+U.

S2. Adsorption geometries of the intermediates in computed reaction pathways Carbene pathway

Fig. S2 shows the adsorption geometries of the intermediates in the carbene pathway. 'TS' means transition states. We observed partial reduction between some intermediates, such as intermediates 12 to 13 (the Lowdin charge difference of HCO is 0.43). For intermediates 2 and 3, although the geometry of CO_2 is changed from linear to bent, this is regarded as a change in adsorption mode, since the same bent CO_2 adsorption can also be observed on neutral anatase(101) without a H atom adsorbed nearby,^{5,6} and therefore is irrelevant to H atom transfer reaction.



















TS







Fig. S2 (Top) Illustration of reaction intermediates in the carbene pathway. (Bottom) Adsorption geometries of the reaction intermediates in the carbene pathway.

Formaldehyde pathway

Fig. S3 shows the adsorption geometries of the intermediates in the formaldehyde pathway.











Fig. S3 (Top) Illustration of reaction intermediates in the formaldehyde pathway. (Bottom) Adsorption geometries of the reaction intermediates in the formaldehyde pathway.

Glyoxal pathway

Fig. S4 shows the adsorption geometries of the intermediates in the glyoxal pathway.









Fig. S4 (Top) Illustration of reaction intermediates in the glyoxal pathway. (Bottom) Adsorption geometries of the reaction intermediates in the glyoxal pathway.

S4. Effect of slab thickness on Fig. 6 in the main manuscript

Our main objective in this study is to identify the most favorable mechanism by comparing three proposed mechanisms, as illustrated in Fig. 6 in the main manuscript. As shown in Fig. S1 the reaction energy changes with the slab thickness, it is therefore deemed necessary to check if the formaldehyde pathway remains as the most favourable mechanism when thicker slab is employed.

Fig. S5 (a) and (b) show Fig. 6 in the main manuscript constructed with 2-layer and 5-layer slab calculations respectively. A comparison between the two shows that the highest-energy intermediate in each pathway remains unchanged, and we would expect the formaldehyde pathway remains as the most favorable pathway. In both cases, H₂CO (4th H transfer, blue) is a favorable 'stepping stone' for CO in the carbene pathway (2nd H transfer, red) and the HCO in the glyoxal pathway (1.5th H transfer, green).

On the other hand, some differences in reaction energies are observed between the two profiles, which are mostly originated from the difference in the adsorption energy of H atom. For instance, the reaction energy of CO₂ to CO (2^{nd} H transfer, red) has ~ 0.5 eV difference. This is similar to the example of HCOOH given in S1, where the difference in the adsorption energy of H atom between 2-layer and 5-layer slab (0.3 eV for one H atom; 0.6 in this case due to two H atoms involved). The reaction energy difference in the two profiles for CO₂ to CH₄ is ~2.2 eV, which is also close to the accumulated difference of 2.4 eV (due to the requirement of 8 H atoms). As discussed, our adsorption energies of H atom with different slab thickness are close to the range of literature values observed (~-2 eV to ~-2.30 eV). Accurate reaction energies are therefore difficult to be determined, due to the uncertainty contained within the reported values of adsorption energy of H atom, subject to the computational method and details, as well as surface coverage.



Fig. S5 (a) Fig. 6 in the main manuscript, constructed with two-layer slab; (b) modified Fig. 6 in the main manuscript, constructed with computations of intermediates based on a 5-layer slab. In both (a) and (b) the intermediates proposed in experiments are labeled in black, while intermediates labeled in blue are suggested in this study.

Reference

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