Supplementary Information for

“A catalytic role of surface silanol groups in CO_2 capture on the amine-anchored silica support”

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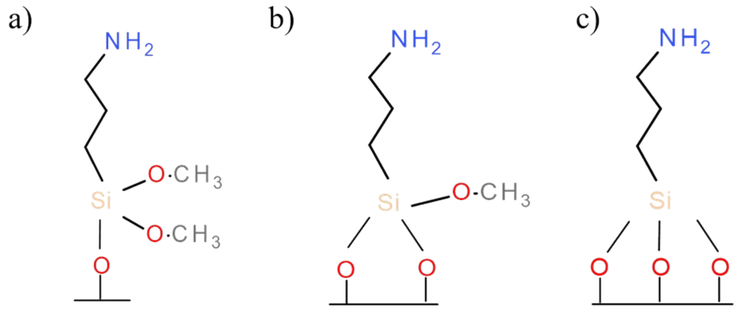
The single chemisorption of APS molecule on the silica surface was examined in order to understand the amine anchoring behaviour and its interaction with the silanols. It is mentioned in the literature that methoxy groups of APS form chemical bond by reacting with silanol groups on the surface, liberating methanol during the reaction, which follows the Eqn. (S-1).[1]

$$\mathrm{APS}_{amine} + \mathrm{Si\text{-}OH}_{slab} \rightarrow \mathrm{Si\text{-}APS}_{slab} + \mathrm{xMethanol} \tag{S-1a}$$

$$\Delta E\ (\mathrm{functionalization}) = E(\mathrm{Si\text{-}APS})_{slab}, + xE(\mathrm{Methanol}) - E(\mathrm{APS})_{amine} - E(\mathrm{Si\text{-}OH})_{slab} \tag{S-1b}$$

The number of chemical bonds APS amine can form with the surface is up to three, which corresponds to the number of methanol generated in the reaction process. Thus amine covalently bonds to the surface (without amine group hydrogen bonding to the silanols on the silica surface), varying the degree of chemical bonds, as shown in Figure S1.

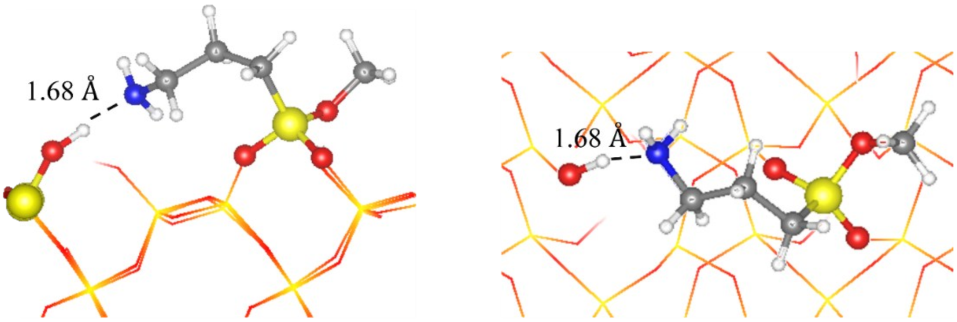


	Single chemical bond anchored (S)	Double chemical bonds anchored (D)	Triple chemical bonds anchored (T)
Functionalization energy (kcal/mol)	-12.3	-16.2	X

Figure S1. Number of bonds APS amine can form with the silica surface and the corresponding functionalization energy.

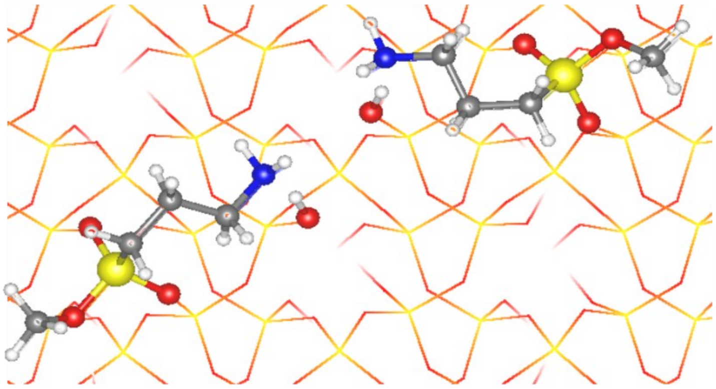
The functionalization energy shows anchoring two bonds on the surface to be the favorable position. Formation of triple chemical bonds with the surface was structurally unfeasible due to the silanols being far apart to form three bonds. Recent computational study on the amine-grafted α-quartz surface had a 'bipodal structure', reacting between aminoalkylethoxysilane and two vicinal silanols.[2] Additionally, a recent experimental study of CO_2 adsorption on amino-organosilane grafted SiO_2 adsorbent has shown the sign of two siloxane bonds formed to the surface through solid state ^{13}C NMR spectrum.[3] Thus, the double anchoring amine structure was used in this study.

Thus, we have considered amine model H-bonding to the surface.due to recent reports showing amine interacting with the surface via H-bonding[4] [5]. The most stable geometry is given in Figure S2.

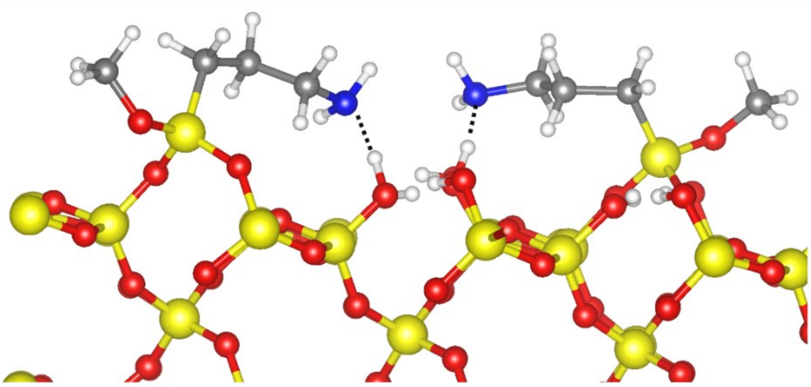


Side view Top view

Figure S2. Optimized geometry of single H-bonded amine from top/side views. Color codes: blue = nitrogen, gray = carbon, yellow= silicon, red = oxygen, white = hydrogen.



Top view



Side view

Figure S3. Optimized geometry of H-bonded dimer amine at top/side views. Color codes: blue = nitrogen, gray = carbon, yellow= silicon, red = oxygen, white = hydrogen.

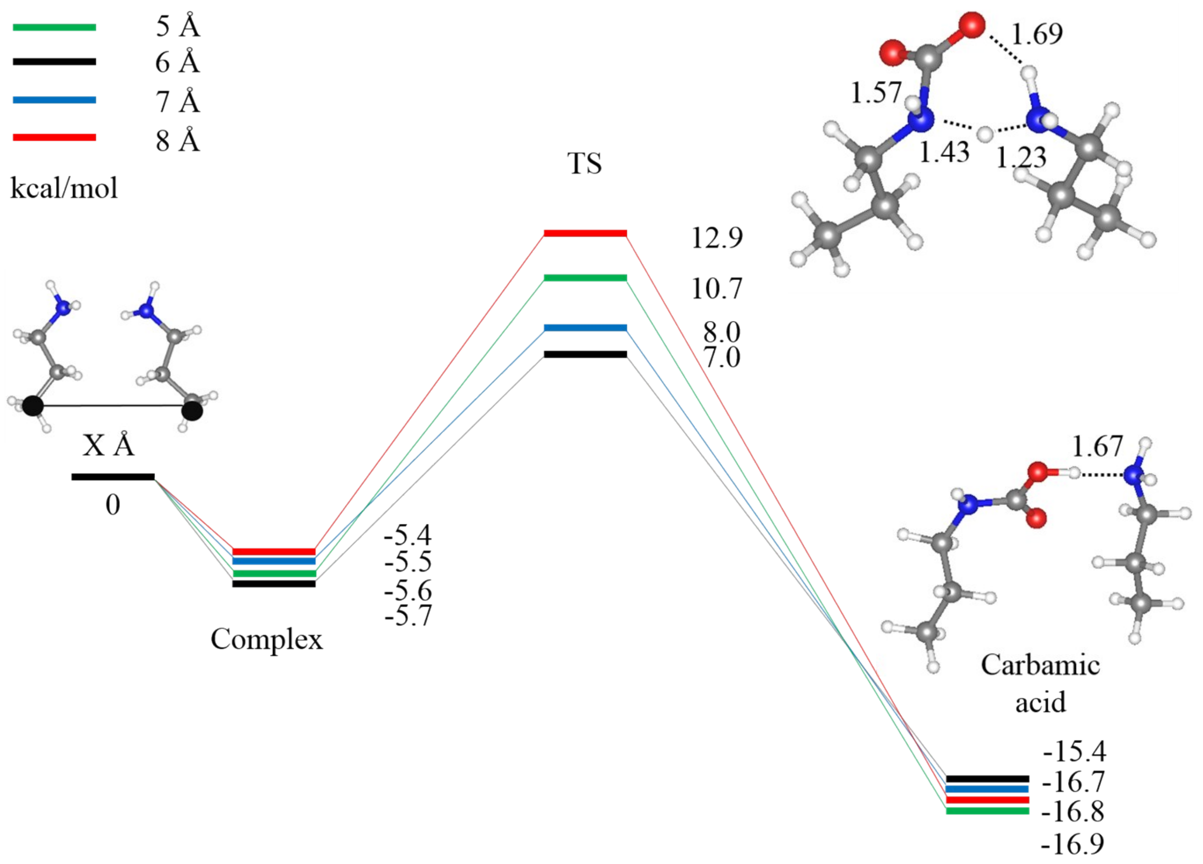


Figure S4. The energy profile of intermolecular mechanism (InterM) for the carbamic acid formation, employing the molecular model. The terminal carbon was fixed (constrained) and the distance of terminal carbon (highlighted in black circle at the reactant image) was varied from 5 to 8Å to find the most favourable InterM distance. Geometries of each state are given at 6 Å as a representative and the energy is in kcal/mol.

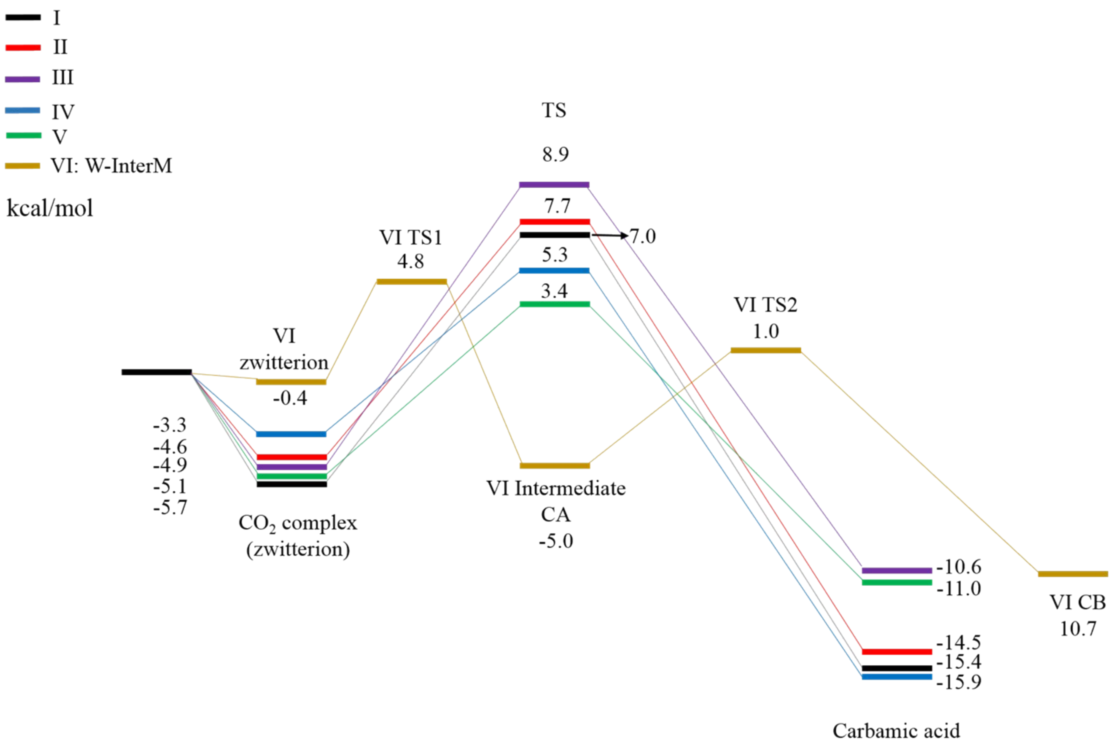
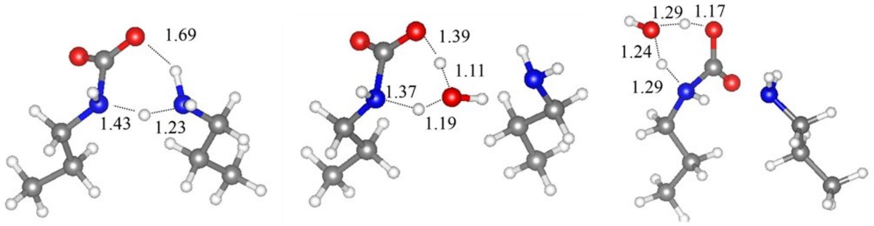


Figure S5. The energy profile of the various InterM pathways for the active role of water molecules as proton transfer bridges for the formation of amine-CO_2 products. The I, II, III, IV, and V paths include a single molecule, when VI:W-InterM Includes two water molecules. The optimized structures are shown in Figure S6. The energy is in kcal/mol.

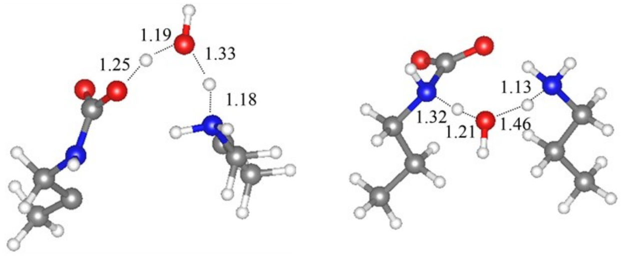
InterM



I – Water-unassisted pathway
$\triangle E^{\ddagger} = 12.7$

II – Intra water bridge
$\triangle E^{\ddagger} = 12.3$

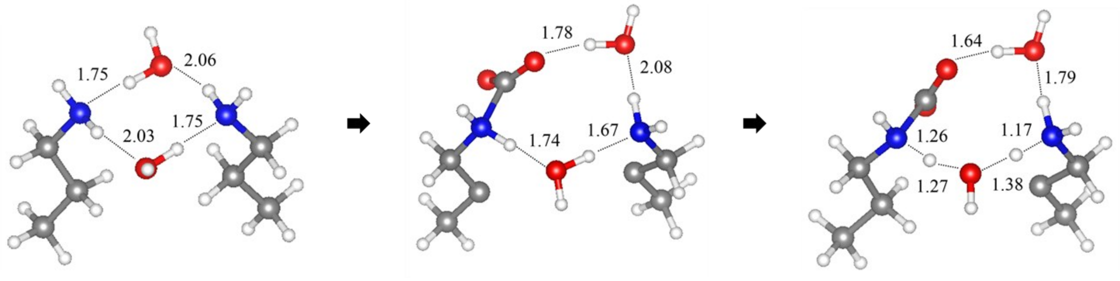
III- Intra water bridge 2
$\triangle E^{\ddagger} = 13.8$



IV – Inter water bridge-1
$\triangle E^{\ddagger} = 8.6$

V – Inter water bridge -2
$\triangle E^{\ddagger} = 8.5$

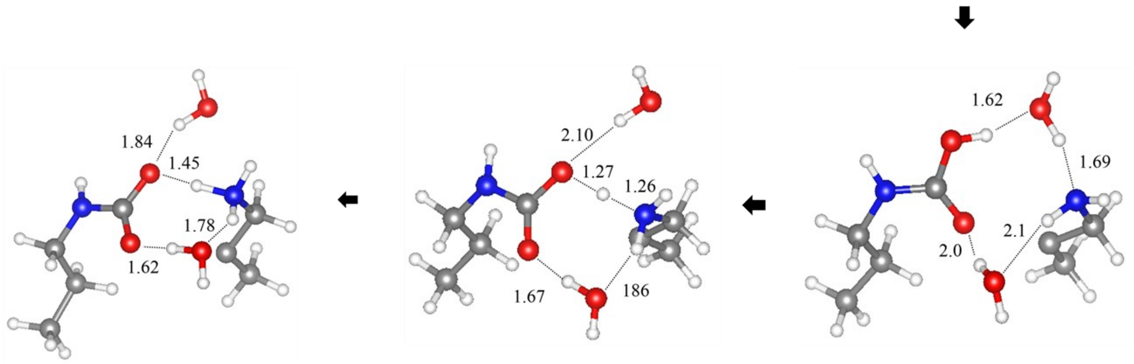
VI - W-InterM



Reference

Zwitterion

TS 1 – Water mediated proton transfer between amines & amine to carboxylic group
$\triangle E^{\ddagger} = 5.2$



Carbamate-Ammonium

TS 2 – Mainly carbonyl & water molecule rearrangement, followed by proton transfer from –COO to amine
$\triangle E^{\ddagger} = 6$

Intermediate
(Carbamic acid)

Figure S6. The transition state structures are shown for path I, II, III, IV, and V. The full molecular representations for the path VI are shown. The $\Delta E^{\ddagger}$ denotes the activation barrier, whereas Inter and Intra denotes Intermolecular and intramolecular, respectively. The energy is in kcal/mol and hydrogen bond lengths are in Å.

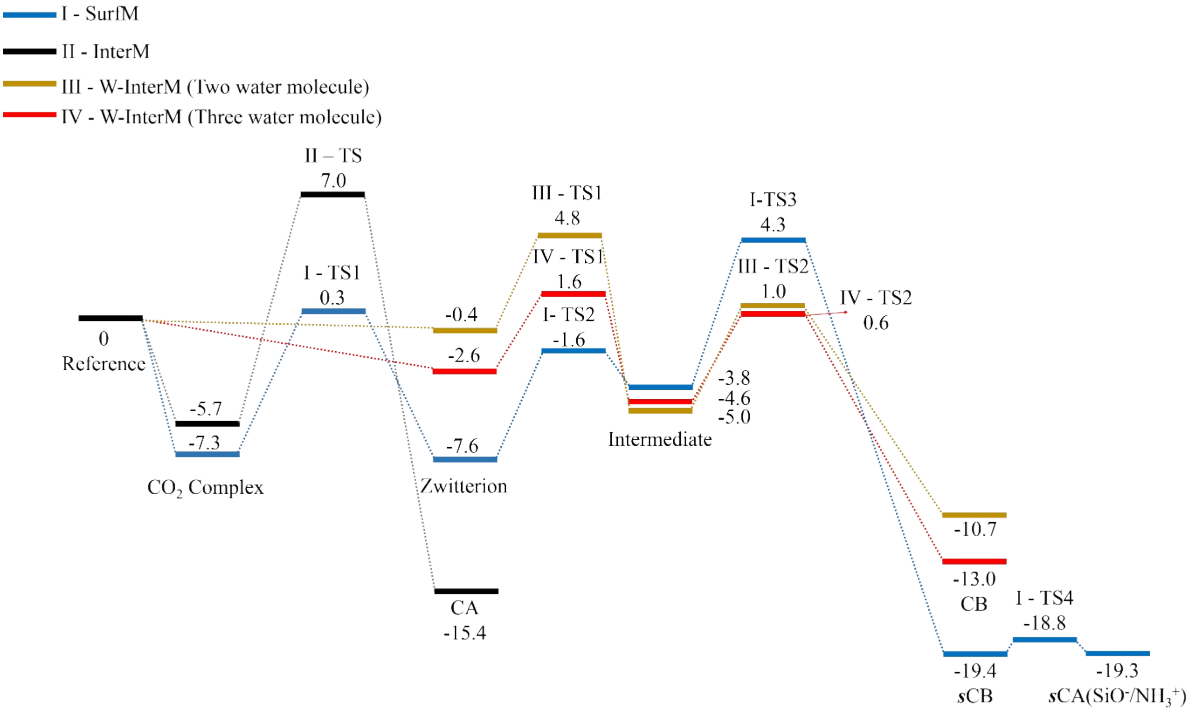
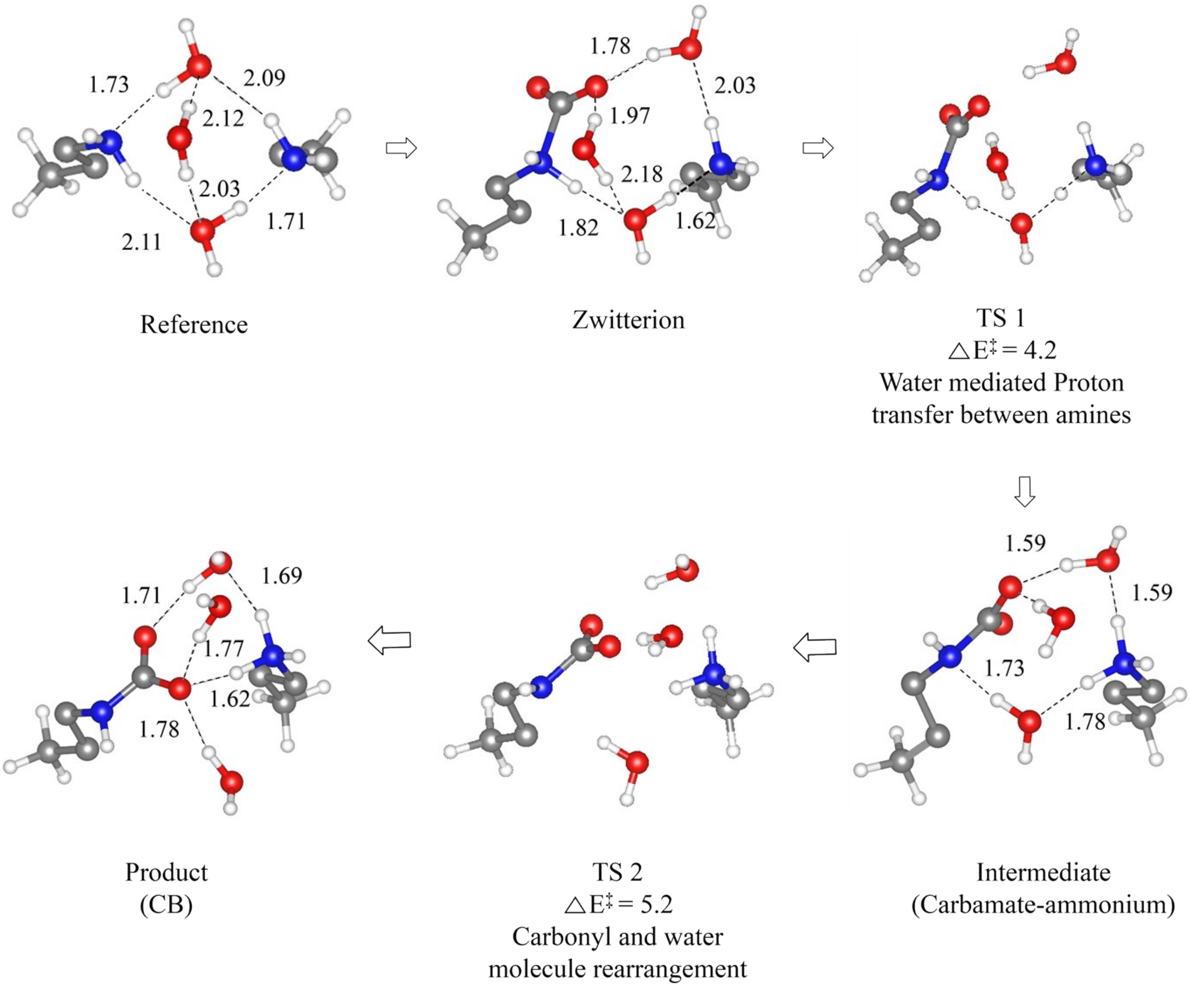


Figure S7. The energy profile of CO_2 binding mechanisms ((surface mechanism (SurfM)), water unassisted InterM (InterM), and water assisted InterM (W-InterM)), with an inclusion of three water molecules path (IV-W-InterM). The energy is in kcal/mol.



Reference

Zwitterion

TS 1
$\triangle E^{\ddagger} = 4.2$
Water mediated Proton transfer between amines

Intermediate
(Carbamate-ammonium)

TS 2
$\triangle E^{\ddagger} = 5.2$
Carbonyl and water molecule rearrangement

Product
(CB)

Figure S8. The optimized structures for three water molecules path are shown. All the energies are in kcal/mol. The $\Delta E^{\ddagger}$ denotes the activation barrier and hydrogen bond lengths are in Å. Some of the hydrogens attached to the backbone carbons are omitted for clarity.

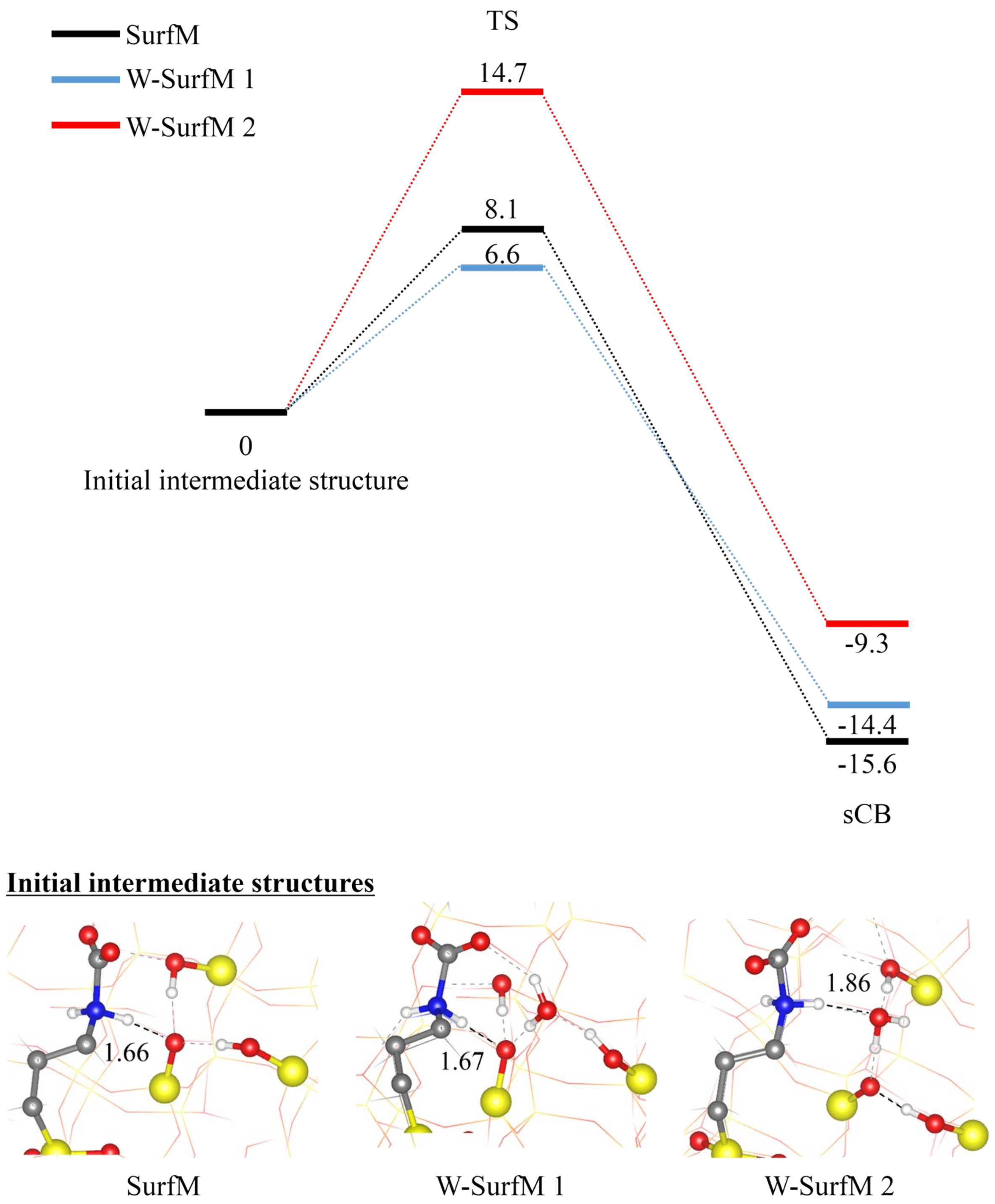


Figure S9. The energy profile for the dry state & water assisted SurfM at the RDS step (step consisting of going from intermediate to sCB product). The water assisted SurfM is denoted as (W-SurfM). The difference between W-SurfM 1 and W-SrufM 2 lies on the orientation of water molecule in the initial intermediate state. Geometries of initial intermediate states are shown above, while full detailed representations are given in Figure S10. All the energies are in kcal/mol.

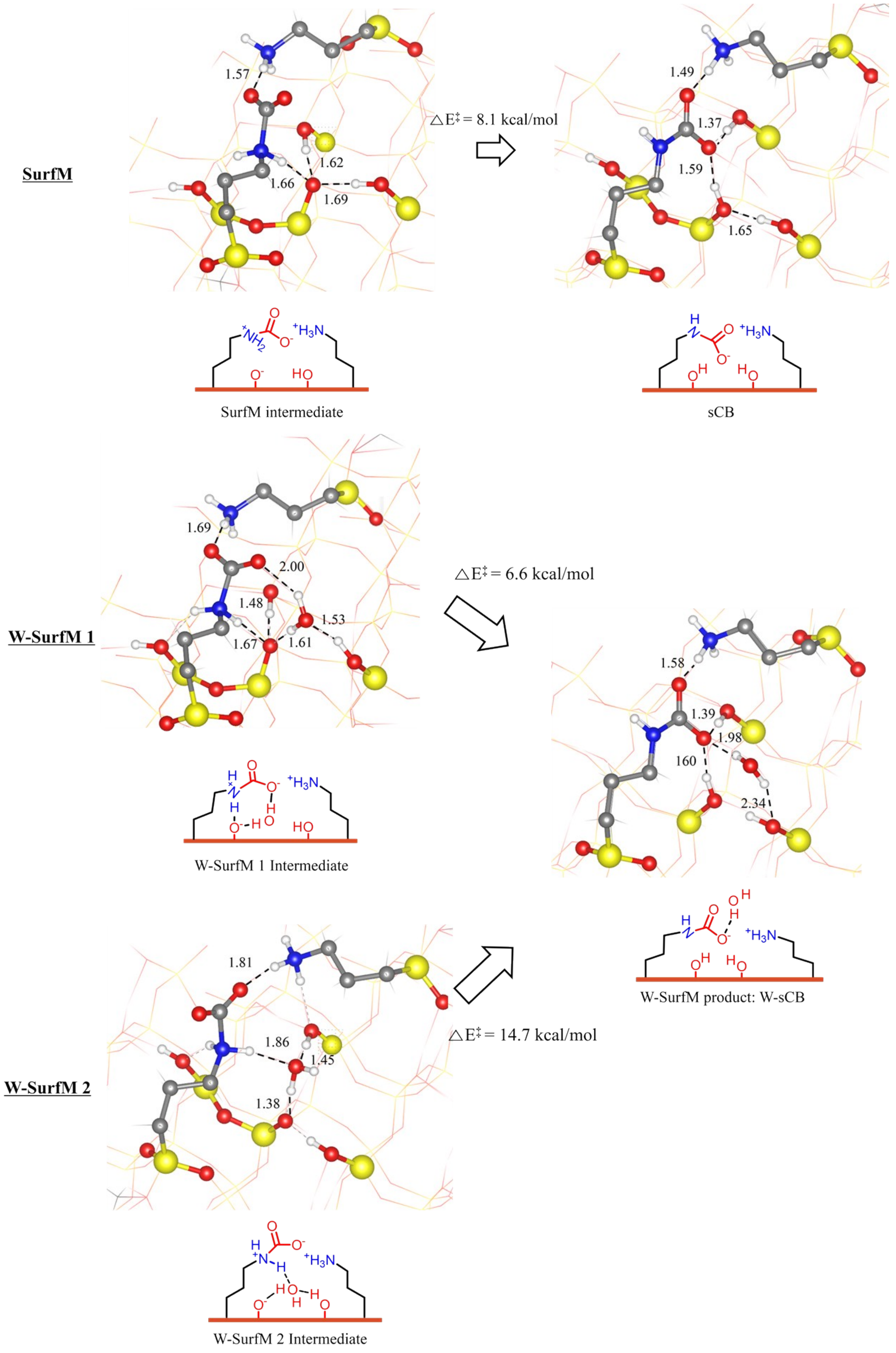


Figure S10. The optimized structures and schematic representations for the initial intermediate/product structures with/without water molecule on SurfM are shown. The ∆E‡ denotes the activation barrier and hydrogen bond lengths are in Å.

References

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2. Kim, K., et al., Molecular Molecular Dynamics Simulations of Aldol Condensation Catalyzed by Alkylamine-Functionalized Crystalline Silica Surfaces. *J. Am. Chem. Soc.* ***2016***, *138*, 7644.-7672

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5. McDonald, T.M., et al., Cooperative insertion of CO_2 in diamine-appended metal-organic frameworks. *Nature*, **2015**, **519**, 303–308