Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

DFT Study on the Mechanism of Photoselective Catalytic Reduction of 4-Bromobenzaldehyde in Different Solvents Employing OH-defected TiO_2 Cluster Model

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Free energy profiles of some unfavourable pathways of Photoselective Catalytic Reduction of 4- Bromobenzaldehyde

The debromination and carbonyl reduction of IM2 in CH_3CN are unfavourable. The free energy profile is depicted in Figure S1.

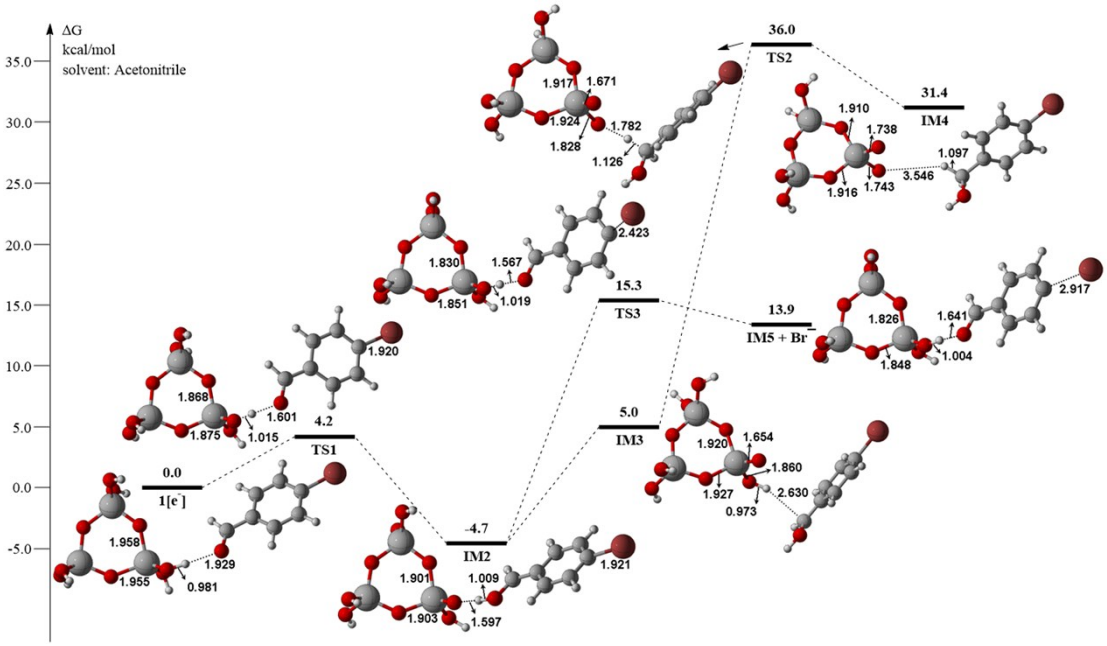

Figure S1: Free energy profile of unfavourable photocatalytic reduction pathway of Bronsted-site adsorbed 4-BBA in CH_3CN. The relative free energies are given in kilocalories per mole while the bond lengths are given in angstrom.

Because of the high barriers and endothermicity, the debromination of 3[e^-] is not dominant. In addition, if the two extra electrons are in pairs, the debromination of 3[$2e^-$] is impossible to occur kinetically (Figure S2).

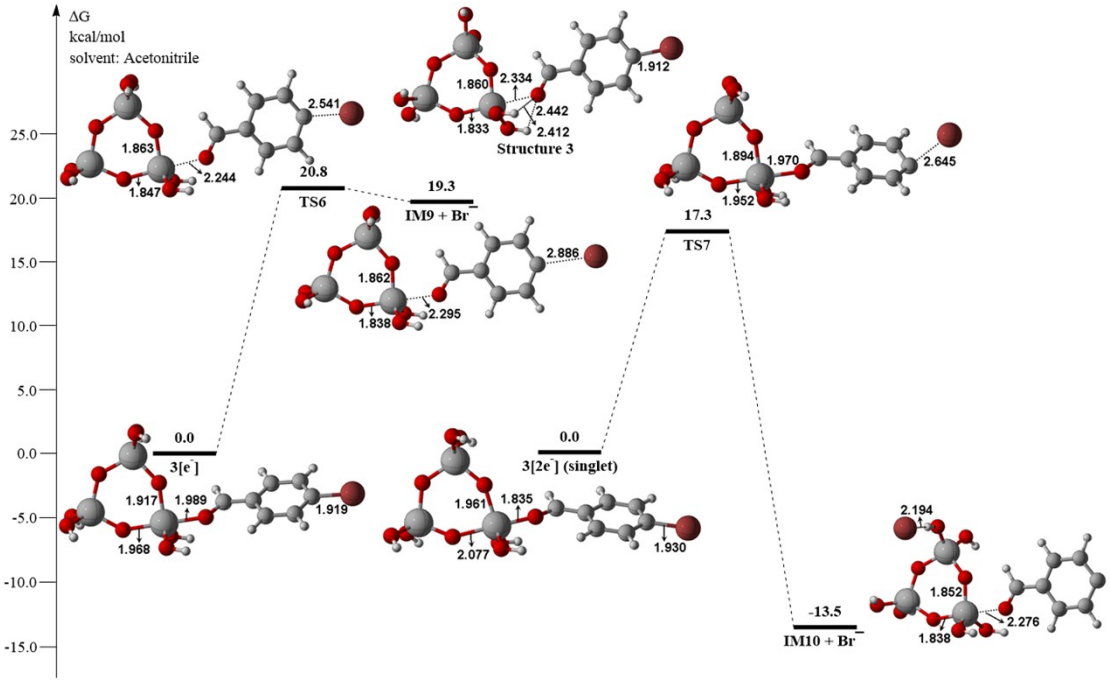

Figure S2: Free energy profile of unfavourable photocatalytic reduction pathway of Lewis-site adsorbed 4-BBA in CH_3CN. The relative free energies are given in kilocalories per mole while the bond lengths are given in angstrom.

The debromination could not compete thermodynamically and kinetically with carbonyl reduction in C_2H_5OH even though the two-electron debromination is effective in CH_3CN (Figure S3).

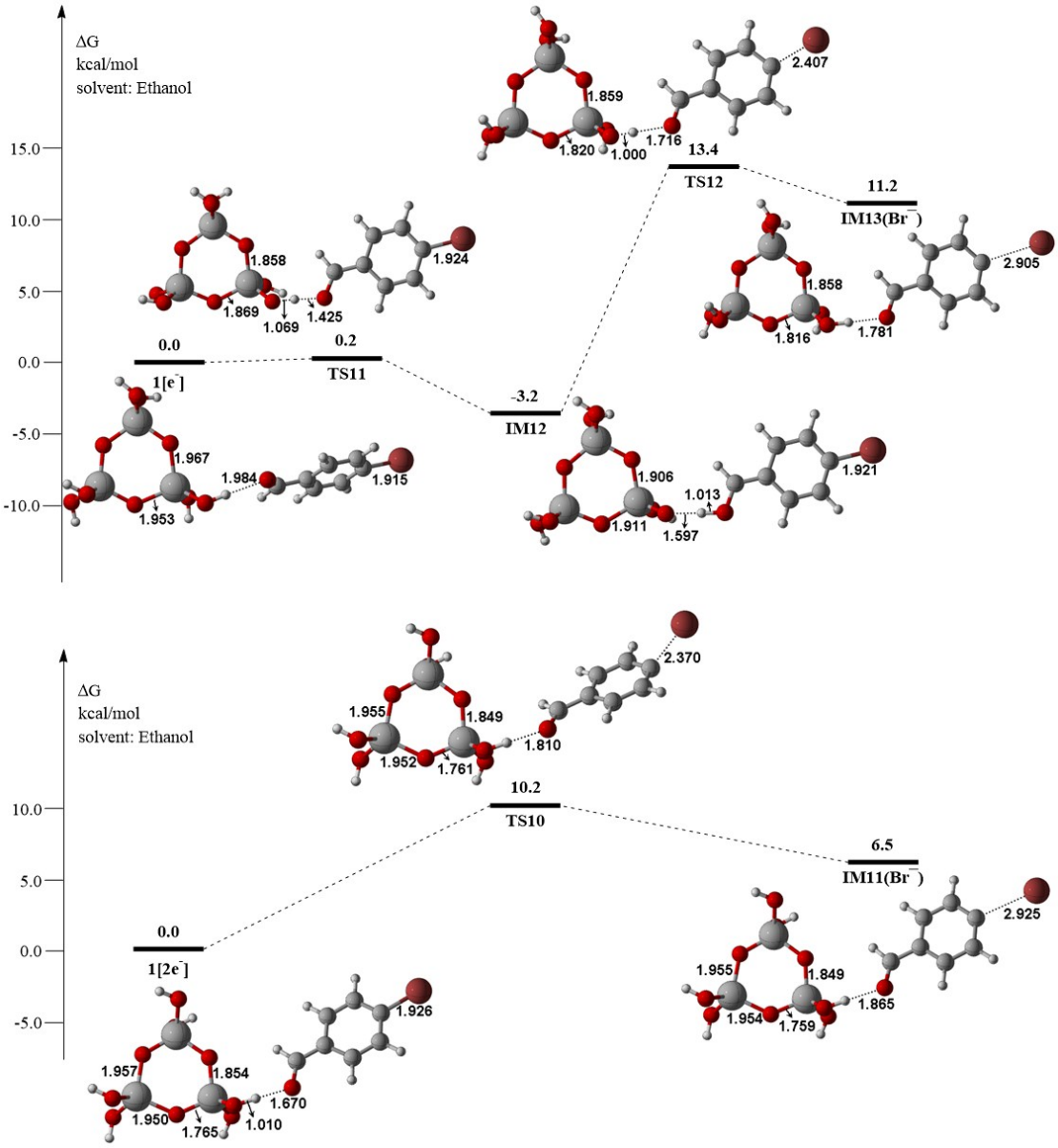

Figure S3: Free energy profile of debromination of Bronsted-site adsorbed 4-BBA in C_2H_5OH without adsorbed solvent molecule. The relative free energies are given in kilocalories per mole while the bond lengths are given in angstrom.

Even though the adsorbed C_2H_5OH could make contribution to transferring the electron from cluster to 4-BBA, the debrominations still have high barriers, which indicates that the debrominations are not the favourable reaction in C_2H_5OH. The free energy profiles are in Figure S4 where TS16, IM19, TS17, and IM20 are not mentioned in Scheme 4.

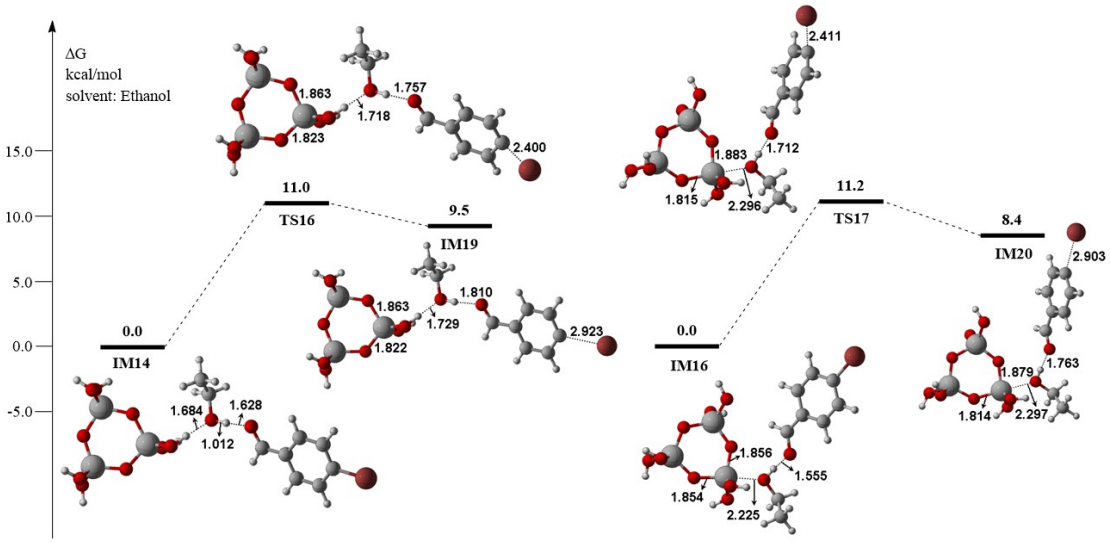

Figure S4: Free energy profile of debromination of adsorbed 4-BBA in C_2H_5OH with Bronsted- and Lewis-site adsorbed solvent molecule. The relative free energies are given in kilocalories per mole while the bond lengths are given in angstrom.

$[Ti_3O_9H_5]^-$ could be recovered by different hydrogen sources, so the complete consumption of OH_cs would not be concerned.

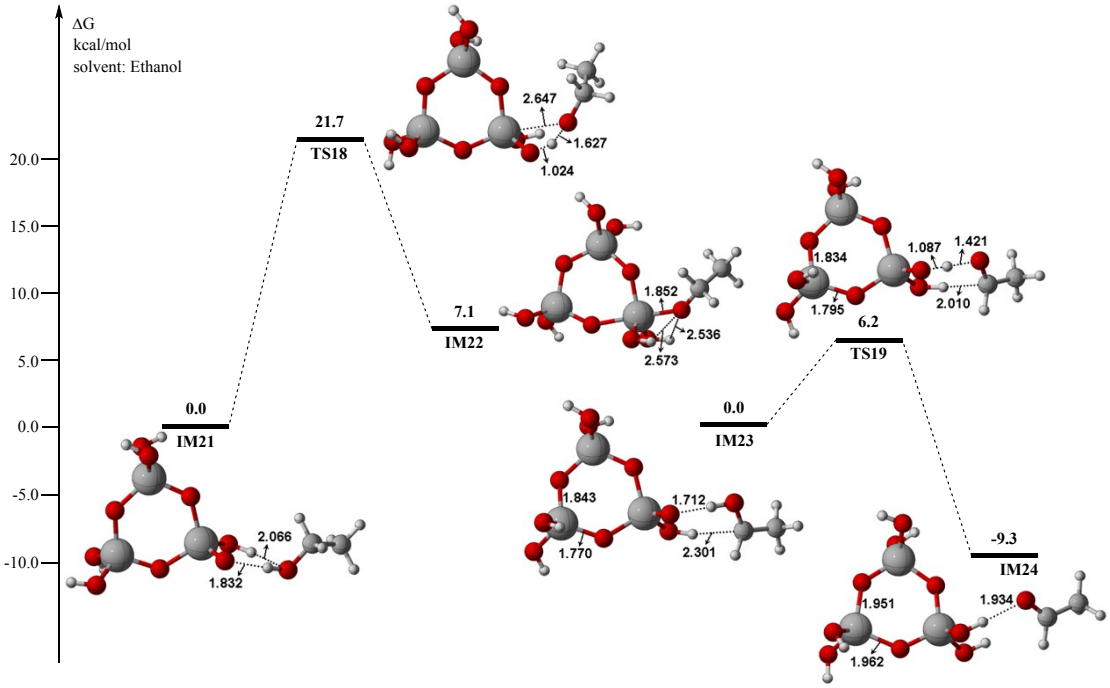

Figure S5: Free energy profile of proton and H atom transfer of $[Ti_3O_9H_5]^-$ in C_2H_5OH through C_2H_5OH and $\bullet CH(CH_3)OH$ radical respectively. The relative free energies are given in kilocalories per mole while the bond lengths are given in angstrom.