Supplementary Infos

S1 Calculation of the different contributions to free energy of a molecule in the gas phase

$Fvib_T$, $Frot_T$, $Ftrans_T$ evaluations The different contributions to free energy $\mathrm{Fvib_T}$, $\mathrm{Ftrans_T}$, $\mathrm{Frot_T}$ of DAE and water are calculated considering a perfect gas.[89]

Fvib is defined as Fvib = ZPE + $\mathrm{Fvib_T}$

Where

$$\mathrm{ZPE} = \mathcal{N}\left(\frac{1}{2}\sum_i h\nu_i\right)$$

$$Fvib_T = \mathcal{N}\sum_i \frac{h\nu_i}{\left(\exp\left(\frac{h\nu_i}{kT}\right)-1\right)} - \mathcal{N}\,kT\left[\sum_i \frac{\left(\frac{h\nu_i}{kT}\right)}{\left(\exp\left(\frac{h\nu_i}{kT}\right)-1\right)} - \ln\left(1-\exp\left(\frac{-h\nu_i}{kT}\right)\right)\right]$$

where $\mathcal{N}$ is the Avogadro number, k the Boltzmann constant, T the temperature, h the Planck constant, and ν_i the vibrational modes.

The rotational free energy contribution of each reactant/product in the gas phase (water and DAE) was calculated with the formula:

$$Frot_T = \mathcal{N}\,kT\left\{\frac{3}{2} - \left[\ln\left(\frac{\sqrt{\pi}}{\sigma}\left(\frac{8\pi^2 kT}{h^2}\right)^{3/2}\sqrt{A_e\times B_e\times C_e}\right)+\frac{3}{2}\right]\right\}$$

where σ is a symmetry number, and A_e, B_e, C_e are inertial moments with respect to the molecule axis.

The translational free energy of each reactant/product in the gas phase (water and DAE) was calculated with the Sackur-Tetrode formula.[90-92]

$$Ftrans_T = \mathcal{N}\,kT\left[\frac{3}{2} - \left(\ln q_t + 1 + 3/2\right)\right]$$

where

$$q_t = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\frac{k_B T}{P}$$

where m is the molecule (DAE or water) mass.

We calculated, in eV, in standard conditions (T = 298K and P = 1 atm)

	TiO_2-4H_2O	DAE^{gas}	$H2O^{gas}$
ZPE	2.96	2.91	0.55
$Fvib_T$	0.32	0.08	0.04
$Frot_T$		-0.28	-0.11
$Ftrans_T$		-0.46	-0.41

S2 Thermal Contributions to Free Energy of the adsorbed DAE molecule

When the ‘surface’ includes an adsorbate, G(surf) can be decomposed in two components, G(mol-ads) and G(surf-noads). G(surf-noads) is the contribution of the surface without adsorbate and G(mol-ads) the contribution of the adsorbed molecules. To evaluate free energy balance before and after adsorption, we consider only variations of the component G(surf) = G(mol-ads), which means that the properties of the adsorbed molecule (vibrational, rotational and translational) are taken into account but not variations of free energy of the bulk phase (TiO_2). In this context, for each adsorbed molecule, we consider that Frot(mol-ads)$_T$ = 2/3 Frot(mol)$_{T,gas}$ when this molecule has no nearest neighbor in the same [010] row and otherwise Frot(mol-ads)$_T$ = 0; thus Frot(mol-ads)$_T$ = 2/3Frot(mol)$_{T,gas}$, Frot(mol-ads)$_T$ = 4/3Frot(mol)$_{T,gas}$, Frot(mol-ads)$_T$ = 2/3Frot(mol)$_{T,gas}$ and Frot(mol-ads)$_T$ =0 for one, two, three and four adsorbed molecules per cell, respectively. Then we write ΔFrot$_{ads}$ = Frot(mol-ads)$_T$ - Frot(mol)$_{T,gas}$

Similar considerations are valid for the Ftrans(surf) term. In this case, the translational free energy of adsorbed DAE molecules are calculated considering that Ftrans(mol-ads)$_T$ = 2/3 Ftrans(mol)$_{T,gas}$ for DAE molecules adsorbed at low coverages (1.28 and 2.56 molecule/nm^2), and zero in all other cases. Then we write ΔFtrans$_{ads}$ = Ftrans(mol-ads)$_T$ - Frot(mol)$_{T,gas}$. For DAE substituting water molecules, the translational energy is zero.

Table SI: Calculated values (in eV) of the vibrational, translation al and rotational free energies of the different configurations considered. 'Ads' refers to DAE adsorbed above a water layer. "Subst" refers to DAE adsorbed in substitution of water molecules.

System and coverage (molecule/m^2)	Fvib(T) (ads)	Frot(ads)	Ftrans(ads)
DAE Ads θ=1.28	0.46	-0.18	-0.30
2 DAE Ads θ=2.56	0.65	-0.37	-0.61
3 DAE ads θ=3.84	0.82	-0.18	0
4 DAE Ads θ=5.12	1.09	0	0
DAE subst θ=1.28	0.28	0	0
2 DAE subst θ=2.56	0.32	0	0
3 DAE subst θ=3.84	0.34	0	0
4 DAE on TiO_2 θ=5.12	0.54	0	0

S3 Configurational Entropy

Configurational entropy was also considered for each DAE coverage. For each system, the – TSconfig term to the free energy estimation:

Sconf = k Ln[(N - n)!/(N!n!)] for n sites occupied by DAE over N surface sites.

Applying the Stirling formula yields

$$TSconfig = \mathcal{N}k\mathcal{T}\ \ln\left((1+\frac{n}{N})+\frac{n}{N}\ln(1+\frac{n}{N})\right)$$

TSconfig can thus be estimated per surface area. This value was found to be negligible in the present system.