

Electronic Supplementary Information

Interactions of Limonene and Carvone on Titanium Dioxide Surfaces

Hanyu Fan,^{1†} Elianna S. Frank,^{2†} Douglas J. Tobias,^{2*} and Vicki H. Grassian^{1*}

¹ Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, California 92093, USA. E-mail: vhgrassian@ucsd.edu

² Department of Chemistry, University of California, Irvine, California 92697, USA. E-mail: dtobias@uci.edu

[†] Equally contributed authors

* Corresponding authors.

The ESI contains 7 figures and 2 tables including: Figure S1 is the FTIR spectra of gas-phase limonene at a pressure of 148 mTorr; Figure S2 is the FTIR spectra of gas-phase carvone at a pressure of 52 mTorr; Figure S3 is the FTIR spectra of limonene on SiO₂ surface using the gas phase as the background; Figure S4 and S5 are the FTIR spectra of limonene and carvone under different RH conditions; Figure S6 is the FTIR spectra of water on TiO₂ surface under different pressures; Figure S7 is the density profiles for limonene on each surface; Figure S8 is snapshots of each kind of hydrogen bonding interaction; Figure S9 is the discussion of non-hydroxylated 0.5 ML kink in PMF; Table S1 and S2 are the list of simulations for all classical molecular dynamics and all *ab initio* molecular dynamics.

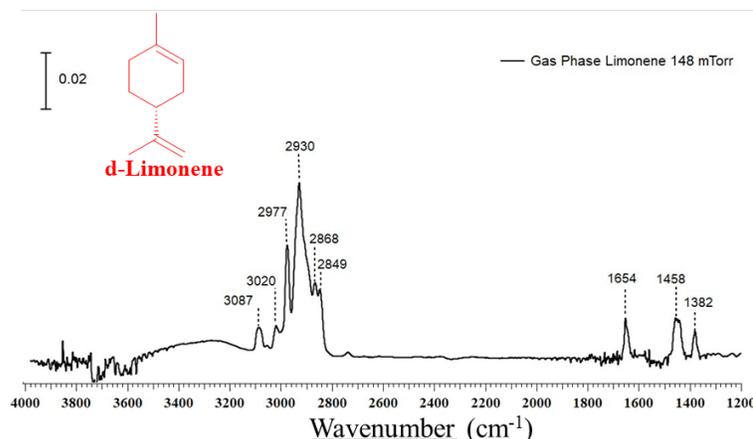


Figure S1. FTIR spectra of 148 mTorr of gas-phase limonene at 296 K in the spectral ranges extending from ca. 1200 to 4000 cm⁻¹ (scale bar = 0.02 absorbance units). The modes are assigned as follows: 3087, 3020 cm⁻¹ for the C-H sp² stretching motion from alkene and ring, respectively; 2977, 2930, 2868, 2849 cm⁻¹ for C-H sp³ stretching motion; 1654 cm⁻¹ for C=C bond stretching vibrations; 1458, 1382 cm⁻¹ for CH₃ and CH₂ bending vibrations, respectively.

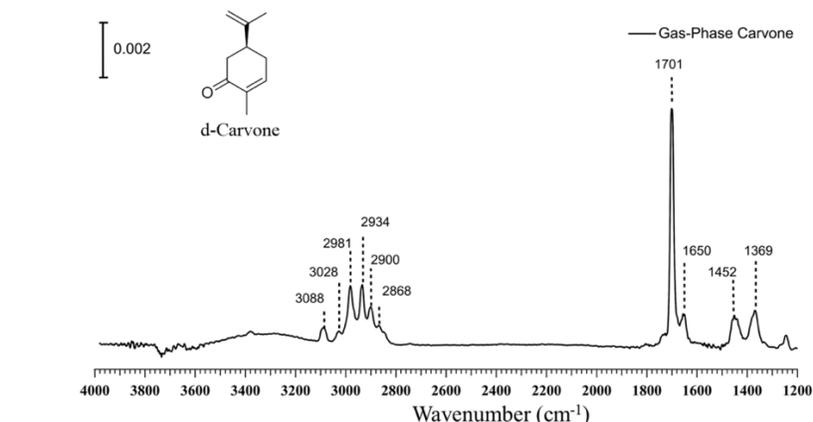


Figure S2. FTIR spectra of 52 mTorr of gas-phase carvone at 296 K in the spectral ranges extending from ca. 1200 to 4000 cm^{-1} (scale bar = 0.002 absorbance units). The modes are assigned as follows: 3088, 3028 cm^{-1} for the C-H sp^2 stretching motion from alkene and ring, respectively; 2934, 2900, 2868 cm^{-1} for C-H sp^3 stretching motion; 1701 cm^{-1} for C=O stretching motion of the carbonyl group; 1650 cm^{-1} for C=C bond stretching vibrations; 1452, 1369 cm^{-1} for CH_3 and CH_2 bending vibrations, respectively.

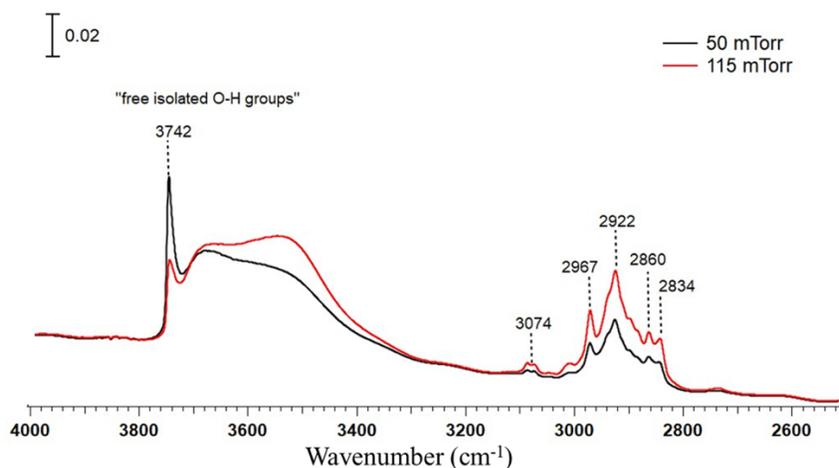


Figure S3. The FTIR spectra of limonene adsorbed on SiO_2 (Degussa Aerosol OX 50) at an equilibrium pressure of 50 and 115 mTorr under dry conditions, respectively (scale bar = 0.002 absorbance units). The IR absorbance spectra are using the gas phase as the background. The peaks at 3742 cm^{-1} means that the free isolated OH function groups on SiO_2 surface are still available at a high equilibrium pressure of 115 mTorr limonene. However, there is almost no free OH function groups available on TiO_2 surface after 42 mTorr limonene adsorption (see Figure 1(b)).

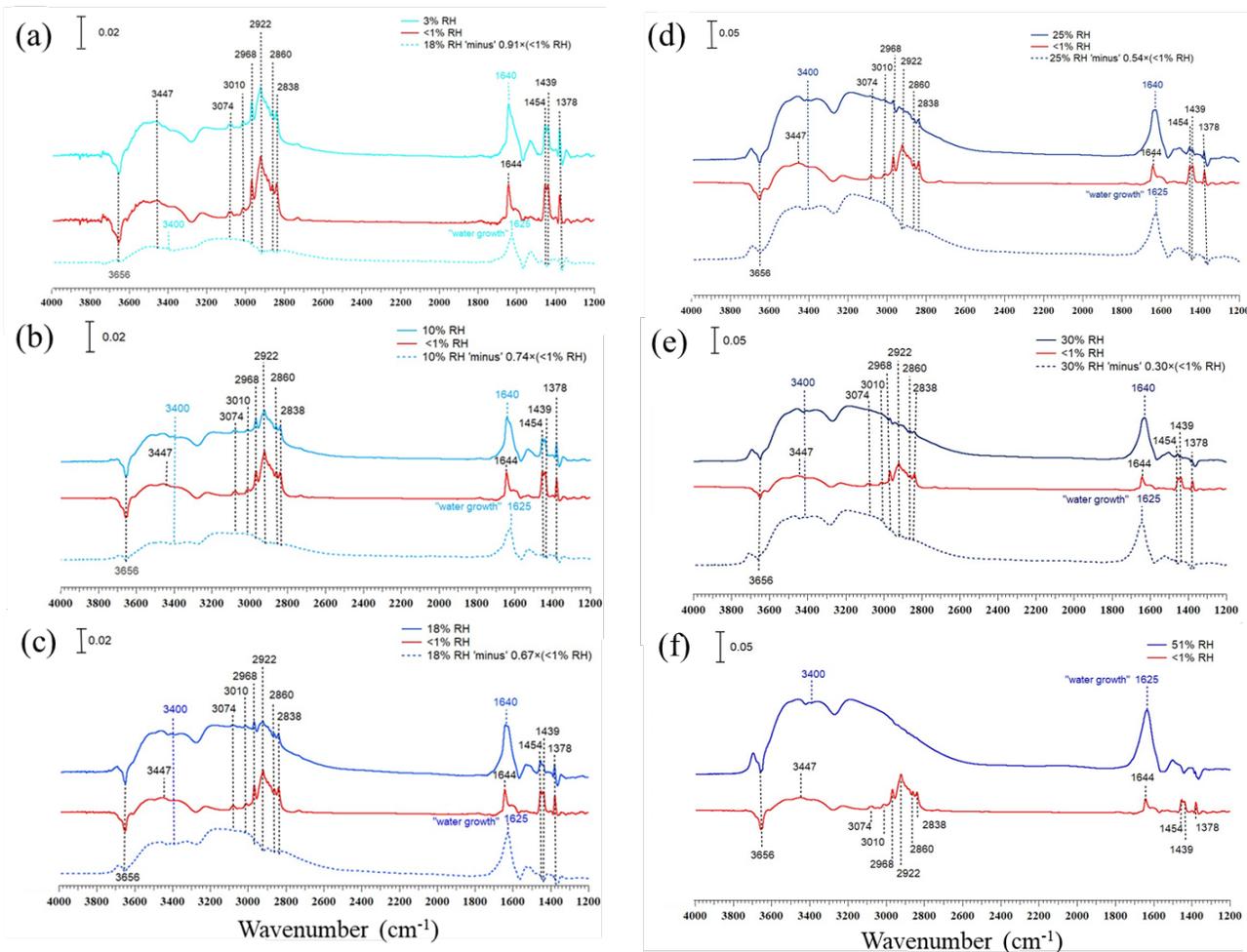


Figure S4. The FTIR spectra of limonene adsorbed on TiO_2 (about 8 mg) surface at an equilibrium pressure of 55 ± 1 mTorr under different RH conditions. The RH is increased in the following increments: < 1%, (a) 3% (scale bar = 0.02 absorbance units), (b) 10% (scale bar = 0.02 absorbance units), (c) 18% (scale bar = 0.02 absorbance units), (d) 25% (scale bar = 0.05 absorbance units), (e) 30% (scale bar = 0.05 absorbance units), (f) 51% (scale bar = 0.05 absorbance units). In each subfigure, the red spectrum is the FTIR spectra of limonene adsorbed on TiO_2 surface under <1% RH condition; the blue solid spectrum is the FTIR spectra of limonene adsorbed on TiO_2 surface under high RH condition; and the dashed blue spectrum is obtained by blue solid spectrum minus the red spectrum with a ratio of the percentage of limonene left on TiO_2 surface as listed in Table 1 to remove the limonene remaining on the hydrated TiO_2 surface from the spectrum so the increase in the adsorbed water absorption bands on the TiO_2 surface under high RH condition can be determined. The broad absorption band centered at around 3400 and the adsorption band at 1625 cm^{-1} in the blue dashed spectra are assigned to the O-H stretching and H_2O bending vibration modes, respectively, for adsorbed water on the TiO_2 surface.

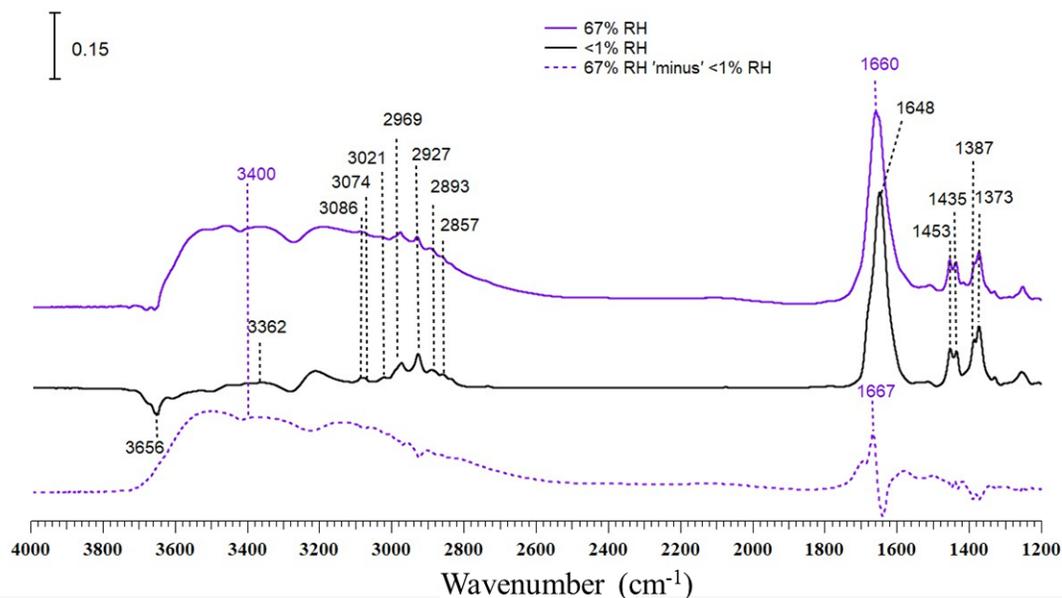


Figure S5. FTIR spectra of carvone adsorbed on TiO₂ (about 8 mg) surface at an equilibrium pressure of 16 mTorr at <1% RH (black solid line) and 67% RH condition (purple solid line), that the peak at 1648 cm⁻¹ shifts to 1660 cm⁻¹ is attributed to the bending mode vibration for adsorbed H₂O. The dashed purple spectrum is obtained by the purple solid spectrum minus the black solid spectrum to show “water growth” on the TiO₂ surface. (scale bar = 0.1 absorbance units)

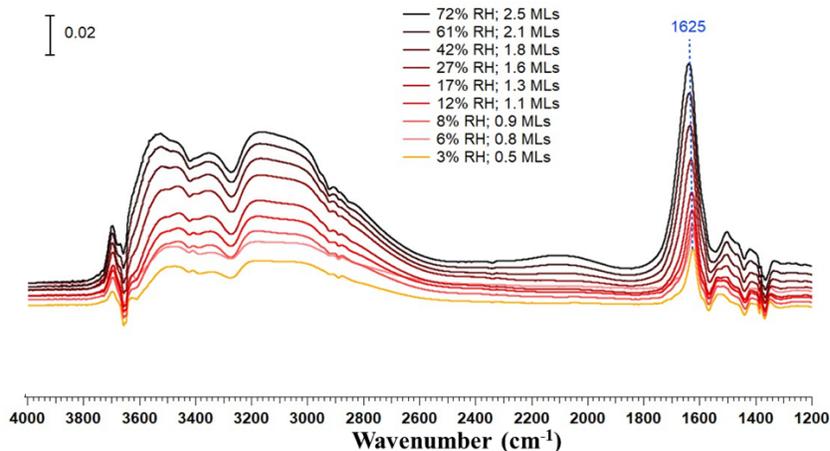


Figure S6. The FTIR spectra of water adsorbed on bare TiO₂ (about 8 mg) surface as a function of pressure ranging from 3% to 72% relative humidity, corresponding to ca. 0.5 to 2.5 MLs (water coverage in monolayers) as determined in Goodman et al.¹ The number of the adsorbed water coverage in monolayers is assumed to be a linear function of the integrated absorbance of the water bending modes at peak 1625 cm⁻¹. The closest RH condition when compared to the Figure S4 (a-f) and S5 is selected as a reference to estimate water MLs on the limonene and carvone adsorbed TiO₂ surfaces, respectively, using the data from Goodman et al¹ for the bare surface.

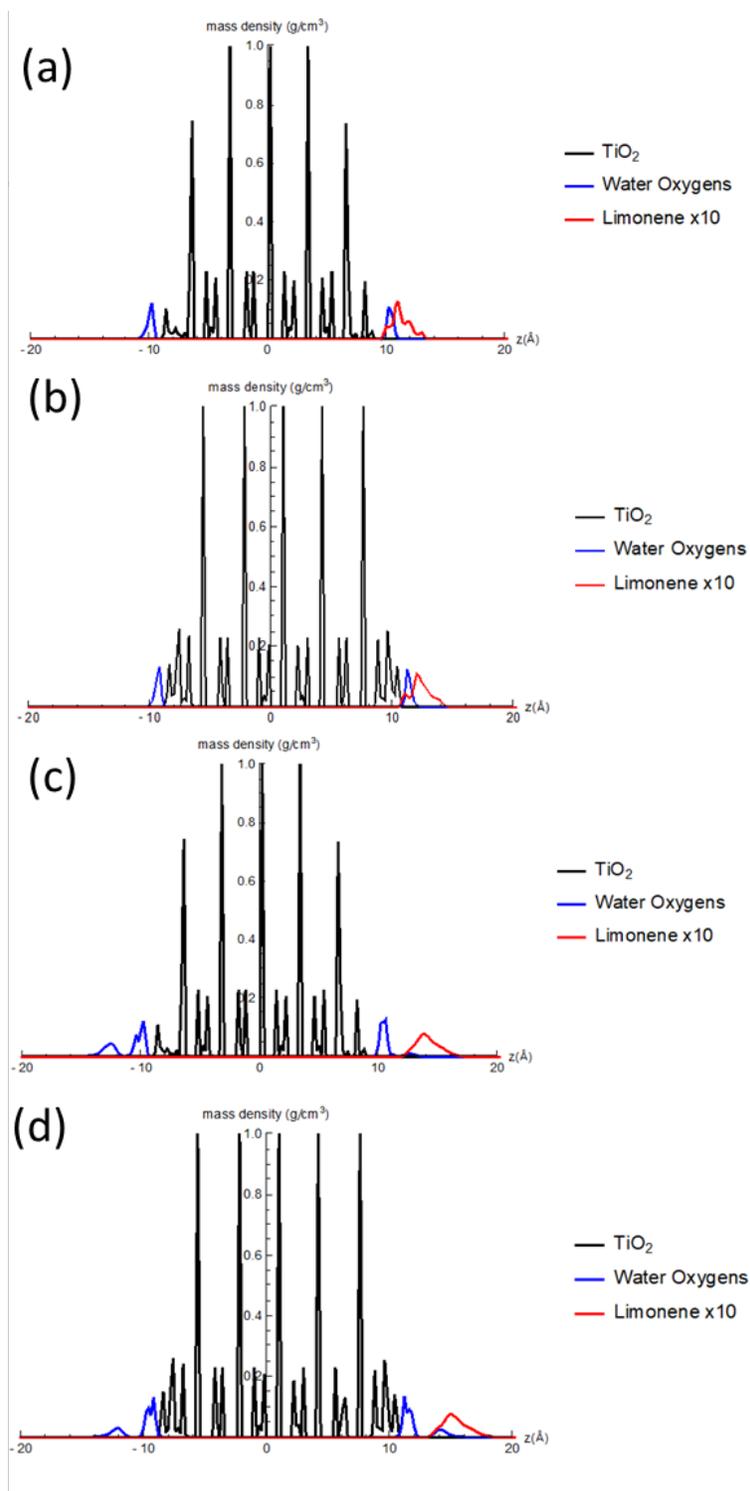


Figure S7. Density profiles for classical molecular dynamics unbiased simulations for limonene (where limonene has been magnified by 10). (a) non-hydroxylated with 0.5 ML (b) -hydroxylated with 0.5 ML (c) non-hydroxylated with 1 ML (d) hydroxylated with 1 ML

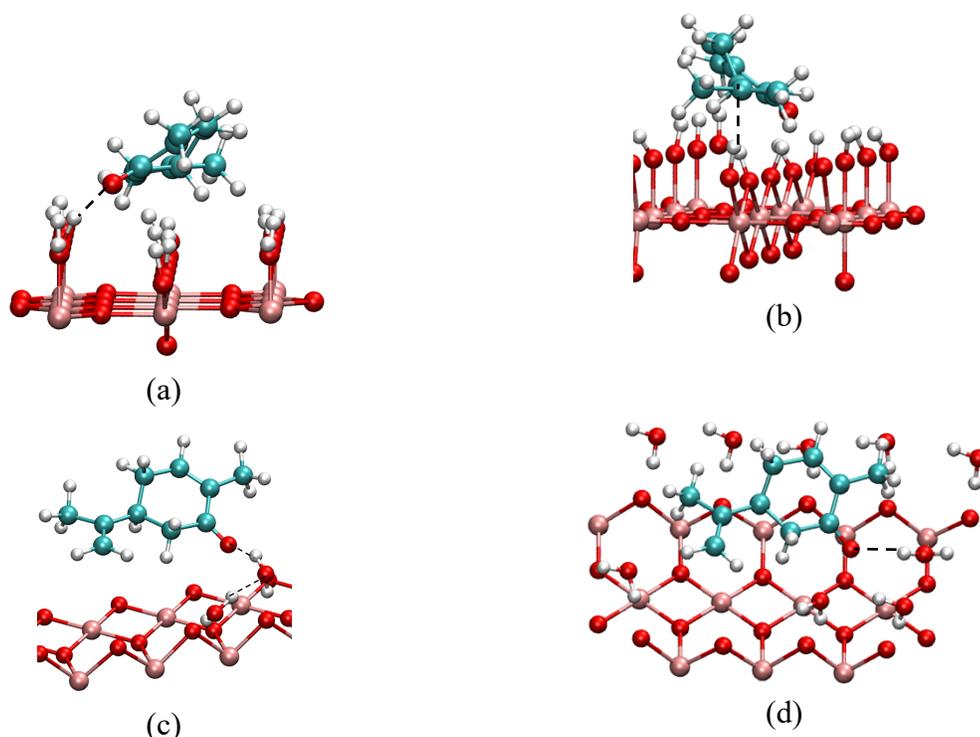


Figure S8. Snapshots of each kind of hydrogen bonding interaction. (a) Carvone oxygen atom in a hydrogen bond with hydroxylated TiO₂ surface. (b) Carvone c_{sp^2} carbon atom in π -hydrogen bond with hydroxylated TiO₂ surface. (c) Carvone oxygen atom in a hydrogen bond with water, where the water molecule is also forming a hydrogen bond with the surrounding water molecules. (d) Carvone oxygen atom in a hydrogen bond with water, where the water molecule is *not* forming a hydrogen bond with the surrounding water molecules.

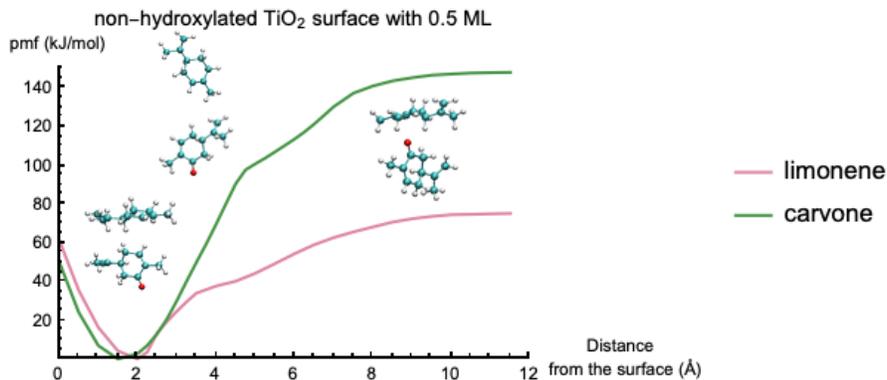


Figure S9. PMF of carvone and limonene on the non-hydroxylated 0.5 ML surface. There is a noticeable kink in the PMF around ~ 4 Å, which we attribute to the endocyclic C=C bond in limonene and the carvone oxygen atom forming hydrogen and π -hydrogen bonds with water molecules of the top of the water layer. This can be seen in the molecular snapshots roughly along the PMF. Additional sampling was done at windows close to 4 Å to ensure all configurations along the PMF were properly sampled. This kink is not seen in the 1 ML and hydroxylated systems due to the full hydration of the surface layer of TiO₂ that allows for the water to form more consistent monolayers, allowing for a more uniform desorption from the surface.

Table S1. List of all classical molecular dynamics unbiased simulations

| Referred to in the text | Base Surface | Number of free water molecules | Adsorbate |
|--|-----------------------------------|--------------------------------|-----------|
| Non-hydroxylated surface | Non-hydroxylated TiO ₂ | 0 | Carvone |
| Non-hydroxylated surface | Non-hydroxylated TiO ₂ | 0 | Limonene |
| Non-hydroxylated surface with 0.5 monolayers | Non-hydroxylated TiO ₂ | 204 | Carvone |
| Non-hydroxylated surface with 0.5 monolayers | Non-hydroxylated TiO ₂ | 204 | Limonene |
| Non-hydroxylated surface with 1 monolayer | Non-hydroxylated TiO ₂ | 408 | Carvone |
| Non-hydroxylated surface with 1 monolayer | Non-hydroxylated TiO ₂ | 408 | Limonene |
| Hydroxylated surface | Hydroxylated TiO ₂ | 0 | Carvone |
| Hydroxylated surface | Hydroxylated TiO ₂ | 0 | Limonene |
| Hydroxylated surface with 0.5 monolayers | Hydroxylated TiO ₂ | 204 | Carvone |
| Hydroxylated surface with 0.5 monolayers | Hydroxylated TiO ₂ | 204 | Limonene |
| Hydroxylated surface with 1 monolayer | Hydroxylated TiO ₂ | 408 | Carvone |
| Hydroxylated surface with 1 monolayer | Hydroxylated TiO ₂ | 408 | Limonene |

Table S2. List of all *ab initio* molecular dynamics simulations

| Surface | Ti atoms in base of surface | O atoms in base of surface | Adsorbate |
|---|-----------------------------|----------------------------|-----------|
| Non-hydroxylated surface | 90 | 180 | None |
| Non-hydroxylated surface | 90 | 180 | Carvone |
| Non-hydroxylated surface | 90 | 180 | Limonene |
| Non-hydroxylated surface with 4 water molecules | 90 | 180 | None |
| Non-hydroxylated surface with 4 water molecules | 125 | 250 | Carvone |
| Non-hydroxylated surface with 4 water molecules | 90 | 180 | Limonene |
| Hydroxylated surface | 90 | 180 | None |
| Hydroxylated surface | 90 | 180 | Carvone |
| Hydroxylated surface | 90 | 180 | Limonene |

References

1. A. L. Goodman, E. T. Bernard and V. H. Grassian, *Journal of Physical Chemistry A*, 2001, **105**, 6443-6457.