Electronic Supporting Information

Adsorption of 6-MHO on Two Indoor Surface Materials: SiO_2 and TiO_2

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The ESI contains 4 figures and 2 tables including: Figure S1 depicts the ordinate plots of the normalized integrated peak area of 6-MHO at 1705 cm^{-1}; Figure S2 is the gas phase scan of the energy of 6-MHO as a function of the dihedral angle depicted in Figure 7 of the manuscript; Figure S3 is the full oxygen power spectra for 6-MHO on SiO_2; Figure S4 is the full oxygen power spectra for 6-MHO on TiO_2; Table S1 and S2 are the list of simulations for all classical molecular dynamics and all *ab initio* molecular dynamics.

Supplemental methods descriptions:

For our force-field based MD simulations of TiO_2 surfaces, the surfaces were prepared as followed: A 110 rutile TiO_2 unit cell was replicated in the x, y and z directions to create the initial structure.[1] Due to the outstanding debate over the nature of the interactions of water on the TiO_2 surface, force field-based MD simulations for both a non-hydroxylated TiO_2 surface with surface Ti atoms and a fully hydroxylated TiO_2 with no surface Ti atoms have been prepared.[2-6] A 35 x 40 x 21 $Å^3$ TiO_2 slab was created and 77 Å of vacuum was placed separating the upper and lower surfaces in the z direction. From this initial surface with 720 Ti atoms and 1440 O atoms, the non-hydroxylated and hydroxylated TiO_2 surfaces were produced. For clarity, we can consider all TiO_2 surfaces consisting of two parts, the frozen core Ti and O atoms and the surface atoms. In the case of the non-hydroxylated surface, the surface atoms are the bridging oxygen

atoms and 5-coordinated Ti atoms. In the case of the hydroxylated surface, all atoms on the top and bottom of the surface were hydroxylated, thus the surface atoms are the surface OH groups. The force field produced by Brandt et al. was used for the non-hydroxylated surface.[7] For the hydroxylated surface, the nonbonded parameters were set to 0 for hydrogen and in order to ensure a neutral surface, the partial charge of all hydrogen atoms was set to +0.44175 e. and the O–H group oxygen partial charge was set to -0.80 e. During the course of the simulation, all bulk atoms were frozen, and all surface atoms were allowed to move freely. There were small distortions of the TiO_2 surface, however the general structure of the TiO_2 crystal was retained.

For our force-field based MD simulations of a SiO_2 surface, the surface was prepared as followed: we prepared an amorphous SiO_2 structure by applying an annealing procedure to an alpha-quartz supercell composed of 11 x 11 x 8 units cells. To accommodate periodic boundary conditions, bonds were introduced between the atoms located at the boards of the crystal with their bonding partners located at the opposite surface, as described in our previous work.[8] Upon completion of the annealing process, a 24 x 50 x 50 $Å^3$ slab was selected from the annealed bulk structure, and oxygen atoms were added to ensure all surface Si atoms satisfied tetrahedral coordination. The hydroxylated SiO_2 surface was generated by hydrogenating the surface oxygen atoms that had only one Si-O bond, resulting in a silanol surface density of 6.7 nm^{-2}.

For our AIMD simulations of TiO_2 surfaces, the surfaces were prepared as followed: the base TiO_2 surface containing 90 Ti atoms and 180 O atoms was selected from a portion of the classical MD surface to construct the non-hydroxylated and fully hydroxylated TiO_2 surface, accounting to 5 layers of Ti and O atoms, which was sufficient to allow for ample simulation time (13 ps). Then, for the fully hydroxylated surface, additional OH groups were added to the surface. For the non-hydroxylated surface with 4 water molecules, a slightly larger size in the y

direction of the TiO_2 surface (125 Ti atoms and 250 O atoms) was used. During the course of the simulation, the bottom half of the TiO_2 surface was frozen.

For our AIMD simulations of SiO_2 surfaces, the surfaces were prepared as followed: a cluster from the force-field MD simulations was obtained and then fully hydroxylated, resulting in a $Si_{23}O_{66}H_{40}$ cluster. To create the partially dehydroxylated surface, two OH groups from surface Si atoms were removed. Each 3-coordinated Si atom was given an unpaired electron, as described by Anderson et al.[9] All systems were placed in orthorhombic boxes under periodic boundary conditions in the X and Y directions with the Z direction normal to the surface.

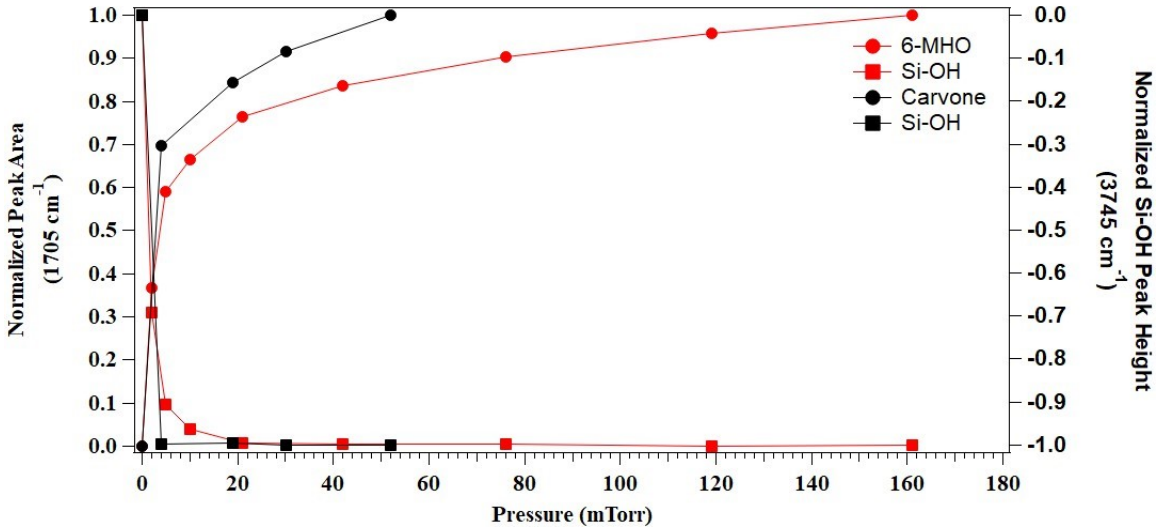

Figure S1. The ordinate plots of the normalized integrated peak area of 6-MHO at 1705 cm^{-1} (ranging from 1640 to 1760 cm^{-1}, red solid circles) compared to the normalized integrated peak area of carvone at 1660 cm^{-1}(ranging from 1500 to 1800 cm^{-1}, black solid circles) as function of pressures (mTorr). The right ordinate plots the normalized peak height of the loss of Si-OH function groups at 3745 cm^{-1} (red solid squares for 6-MHO and black solid squares for carvone). The equilibrium pressures are 2, 5, 10, 21, 42, 76, 119, and 161 mTorr for 6-MHO and 4, 19, 30 and 52 mTorr for carvone, respectively.

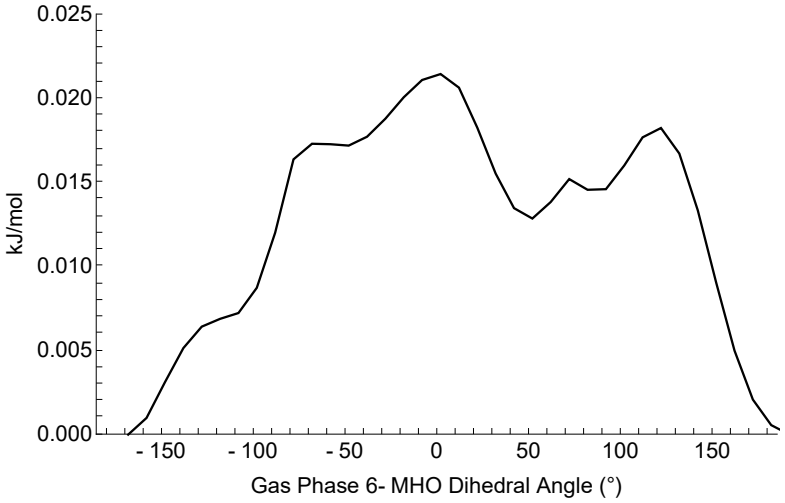

Figure S2. Gas phase scan of 6-MHO dihedral angle depicted in Figure 7 of the manuscript.

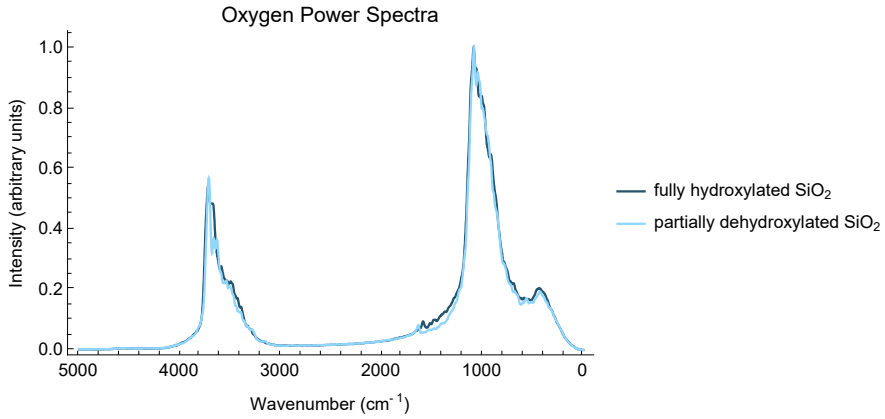

Figure S3. Power spectra for all oxygen atoms for 6-MHO adsorbed on the fully hydroxylated SiO_2 surface and partially dehydroxylated surface. All intensity values have been scaled to run from 0 to 1.

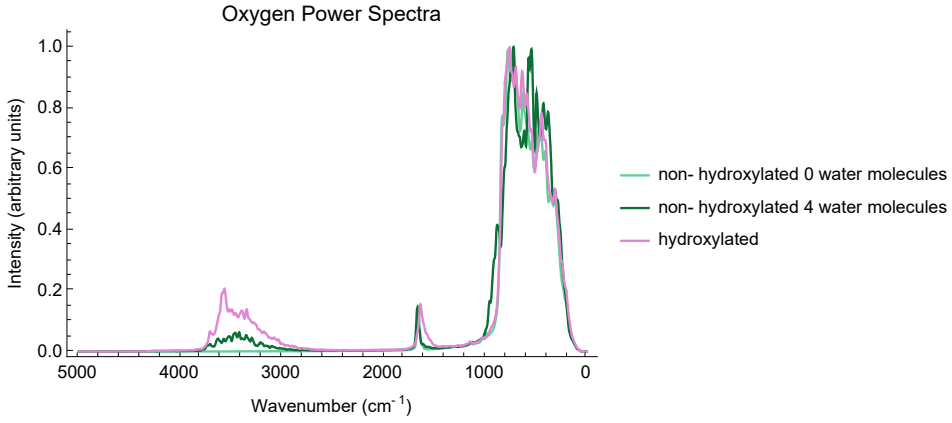

Figure S4. Power spectra for all oxygen atoms for 6-MHO adsorbed on the non-hydroxylated TiO_2 surface with 4 water molecules and for 6-MHO adsorbed on the hydroxylated TiO_2 surface. All intensity values have been scaled to run from 0 to 1.

Table S1. List of all classical molecular dynamics unbiased simulations

Surface	Simulation time
SiO_2	50 ns
Non-hydroxylated TiO_2	50 ns
Hydroxylated TiO_2	50 ns

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

Surface	Functional	Simulation time
Fully hydroxylated SiO_2 cluster	BYLP-D3	40 ps
Partially dehydroxylated SiO_2 cluster	BYLP-D3	16 ps
6-MHO gas phase	BYLP-D3	10 ps
Fully hydroxylated TiO_2 cluster	PBE	20 ps
Non-hydroxylated TiO_2 cluster	PBE	20 ps
Non-hydroxylated TiO_2 cluster with 4 water molecules	PBE	13 ps
6-MHO gas phase	PBE	10 ps

Reference:

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