Supporting Information for

**Water dissociation on the low-coordinated sites of MgO nanopowders**

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**Computational details**

Various systems have been simulated. For the case of mono-atomic steps, we constructed a MgO(510) surface by using shifted periodic boundary conditions [1]. The slab was 5 MgO layers thick, with a void space equivalent to 6 MgO layers. The lateral dimension along the step edge was 3a0, where a0=7.97 bohr is the computed lattice parameter. The slab consists of 150 atoms (75 Mg + 75 O). We studied water adsorption by starting with an educated guess for the hydroxyl groups that relies upon previous results [2, 3]. Either one or three water molecules have been dissociated on each slab side, corresponding to 1/3 or 1/1 step coverage, respectively.

Corners at mono-atomic steps have been simulated by constructing periodic kinks on the steps at MgO(510) or taking away an O and a Mg atom (that is, creating a MgO divacancy) at the step edges. The overall slab dimensions are thus the same as for the MgO(510) surface. We simulated the dissociation of two water molecules, one on each slab side, at the corners.

For the case of diaomic steps, we constructed a MgO(620) surface by using shifted periodic boundary conditions [1]. The slab was 7 MgO layers thick, with a void space equivalent to 6 MgO layers. The lateral dimension along the step edge was 3a0. The slab thus constructed consisted of 168 atoms (84 Mg + 84 O). Corners have been simulated through the use of shifted boundary conditions along the edge, as in the case of mono-atomic steps. Two water molecules (one on each slab sides) have been adsorbed starting from several non-equivalent configurations, which we constructed by using the results of dynamical simulations of water dissociation on smaller slabs.

In all cases, the central innermost MgO layer was kept fixed in the ideal crystal position, and the distance between the periodic images of the adsorbed hydroxyls on the two slab sides was kept larger than 10 Angstroms. We used the Gamma point for sampling of the Brillouin zone. By running selected tests with bigger void space and finer k-point sampling, we checked that the computed O-H stretching frequencies did not vary within a few cm-1.

**Table**: The main characteristics of the simulations.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| System | Slab thickness | Void size (equivalent number of layers) | Number of Mg or O atoms | Number of water molecules |
| MgO(510) | 5 MgO layers | 6 MgO layers | 150 | 0 |
| MgO(510) + H2O(1/3 step coverage) | 5 MgO layers | 6 MgO layers | 156 | 1+1 (on both slab sides) |
| MgO(510) + H2O(full step coverage) | 5 MgO layers | 6 MgO layers | 168 | 3+3 (on both slab sides) |
| MgO(510) + VMgO | 5 MgO layers | 6 MgO layers | 146 | 0 |
| MgO(510) + VMgO + H2O | 5 MgO layers | 6 MgO layers | 152 | 1+1(on both slab sides) |
| MgO(510) + kink | 5 MgO layers | 6 MgO layers | 150 | 0 |
| MgO(510) + kink + H2O (1/3 step coverage) | 5 MgO layers | 6 MgO layers | 156 | 1+1 (on both slab sides) |
|  |  |  |  |  |
| MgO(620)  | 7 MgO layers | 6 MgO layers | 168 | 0 |
| MgO(620) + corner | 7 MgO layers | 6 MgO layers | 168 | 0 |
| MgO(620) + corner + H2O@corner | 7 MgO layers | 6 MgO layers | 174 | 1+1 (on both slab sides) |

**REFERENCES**

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