Supporting information

For

Water contamination effect on liquid acetonitrile / TiO_2 anatase (101) interface for durable dye-sensitized solar cell

Submitted by

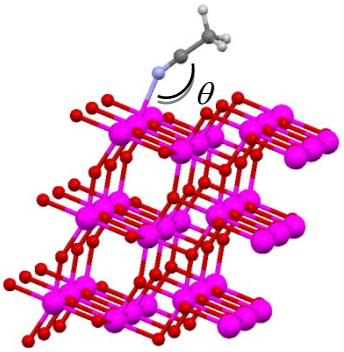
Masato Sumita, Keitaro Sodeyama, Liyuan Han, and Yoshitaka Tateyama

Contents:

1. Optimized structures of MeCN and H_2O on the TiO_2 (101) surface in vacuo

1.1 MeCN on the TiO_2 (101) surface

We have calculated the adsorption energy depending on θ (bond angle of Ti_{5C}-N_A-C_A). Our calculations indicate that there is a minimum around θ=150°. Furthermore, we have obtained the adsorption energy (9.54 kcal mol^{-1}), consistent with the previous Force Filed calculation (12.58 kcal mol^{-1}). The results are summarized in the following table with the 3D picture.

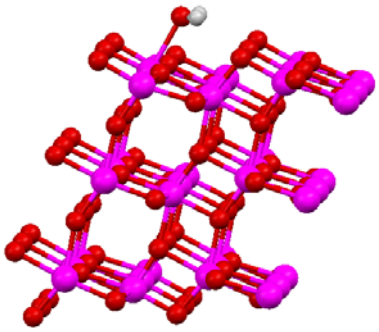


Species	E / E_h	ΔE / kcal mol^{-1}
Dissociated limit	-1311.6813	0.0
θ=120°	-1311.6956	8.96
θ=150°	-1311.6965	9.54
θ=180°	-1311.6962	9.35
Previous calculation[a]	–	12.58

a) F. Schiffman, J. Hutter, J. VandeVondele, *J. Phys.: Condens. Matter* 2008, **20**, 064206(8pp).

1.2 H_2O on the TiO_2 (101) surface

We have obtained the structure comparable to that in the previous calculation (Y. He, et al, *Nature Materials* 2009, **8**, 585-589). The calculated adsorption energy is summarized in the following table with the 3D picture.



Species	E / E_h	ΔE / kcal mol^{-1}
Dissociated limit	-1305.8033	0.0
Adsorbed structure	-1305.8211	11.15
Experimental value[a]	–	11.53-16.14

a) M. Egashira, S. Kawasumi, S. kagawa, and T. Seiyama, *Bull. Chem. Soc. Jpn.* 1978, **51**, 3144.

2. MeCN solvation structures of H_2O molecule in the systems I, II, and III.

The following figures show snapshots of the MeCN solvation structures of H_2O molecule and the radial distribution functions from the water oxygen in the systems I, II and III (C_A. N_A, and H_A correspond to the carbon, nitrogen and hydrogen atoms in MeCN, respectively). The water hydrogen is solvated by the nitrogen in MeCN as well as the surface oxygen, while the methyl group of MeCN, in spite of the hydrophobic nature, mainly coordinates to the water oxygen. This type of solvation structure is attributed to the dipole of the MeCN molecule.