

NANOCLUSTER DFT STUDIES WITH APPLICATIONS TO PRODUCTION AND STORAGE OF HYDROGEN.

G.J. Kroes¹, A. Marashdeh¹, R.A. Olsen¹, O.M. Løvvik², and Z.W. Qu¹

*1: Leiden Institute of Chemistry, Leiden University, Gorlaeus Laboratories, P.O. Box 9502
2300 RA Leiden, The Netherlands*

*2: Centre for Materials Science and Nanotechnology, University of Oslo, P.O. Box 1126
Blindern, N-0318 Oslo Norway, and Institute for Energy Technology, P.O. Box 40, N-2027
Kjeller, Norway*

g.j.kroes@chem.leidenuniv.nl

Cluster studies employing density functional theory (DFT) and relevant to production and storage of hydrogen will be presented.

NaAlH₄ is a promising material for hydrogen storage. Experiments performed by Bogdanovic and Schwickardi (1) have shown that doping the material with Ti makes the uptake and release of hydrogen reversible, also improving the kinetics. However, it is still not clear in which way(s) Ti catalyses the release from and uptake in this material.

We have performed DFT calculations at the generalised gradient approximation (GGA) level to determine what constitutes a good model cluster. A large, geometry optimised semi-spherical cluster exhibiting a (001) surface and consisting of 23 formula units was found to be energetically, electronically, and structurally close to surface and bulk NaAlH₄ (2). Studies on adsorption on and absorption in the cluster of one Ti atom (2), two Ti atoms (3), and TiH₂ (4) show a consistent picture. The energetically preferred situation is obtained if a Ti atom (or Ti atoms) or a TiH₂ “molecule” is exchanged with a surface Na ion (see also Fig.1). This suggests a “zipper model” for Ti-catalysed hydrogen release: Ti (or TiH₂) can eat its way into NaAlH₄ by exchanging with surface Na ions, leading to hydrogen desorption and the formation of the intermediate Na₃AlH₆ and final NaH and Al products.

TiO₂ is a benchmark material for photolytic water splitting, although the band gap of the bulk material (3.0 eV for rutile and 3.2 eV for anatase) is too large to make the bulk material of practical interest for conversion of solar energy to chemical energy in hydrogen (5). We have performed hybrid DFT studies using the B3LYP functional of (TiO₂)_n clusters with n=1-16. Clusters with n=10-16 have a size of approximately 1 nm (6,7). The stablest clusters with n=2-9 generally have terminal Ti=O bonds (singly co-ordinated oxygen atoms) characterised by infrared absorption frequencies in the range 988-1020 cm⁻¹. However, for n=10-16 we have been able to find a number of stable clusters which do not have these Ti=O “defects”. This should be relevant for model studies of photochemistry on TiO₂: our studies of (TiO₂)_n⁺ cations suggest that the hole tends to localise on the least co-ordinated O-atom of the cluster. Clusters with terminal Ti=O bonds would therefore be inappropriate for studies of photochemistry on rutile (110) surfaces, which only exhibit twofold and threefold co-ordinated O-atoms. The clusters with n=10-16 show odd-even oscillations of their electronic properties (see Fig.2). Interestingly, for the clusters with odd n strong interatomic O(2p) lone pair interactions can significantly reduce the lowest vertical excitation energy, to values significantly below the band gap of bulk TiO₂. If materials can be engineered to incorporate such (TiO₂)_n nano-particles, they could exhibit visible light photoactivity.

References:

- (1) B Bogdanovic, M Schwickardi: J. Alloys Comp. 253-254 (1997) 1-9.
- (2) A Marashdeh, RA Olsen, OM Løvvik, GJ Kroes: A density functional theory study of Ti-doped NaAlH₄ clusters. Chem.Phys.Lett. 426 (2006) 180-86.

- (3) A Marashdeh, RA Olsen, OM Løvvik, GJ Kroes: J.Phys.Chem.C (2007) in print.
- (4) A Marashdeh, RA Olsen, OM Løvvik, GJ Kroes: (2007) submitted.
- (5) M Grätzel: Cattech 3 (1999) 4-17.
- (6) ZW Qu, GJ Kroes: Theoretical study of the electronic structure and stability of titanium dioxide clusters $(\text{TiO}_2)_n$ with $n=1-9$. J.Phys.Chem.B 110 (2006) 8998-9007.
- (7) ZW Qu, GJ Kroes: (2007) submitted.

Figures:

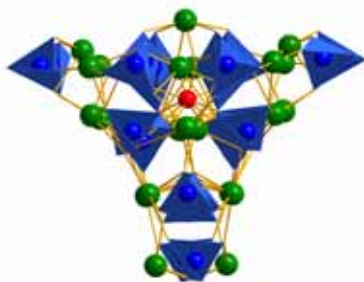


Figure 1.(Color) TiH_2 absorbed in the $Z=23$ cluster: TiH_2 unit exchanged with surface Na ion.

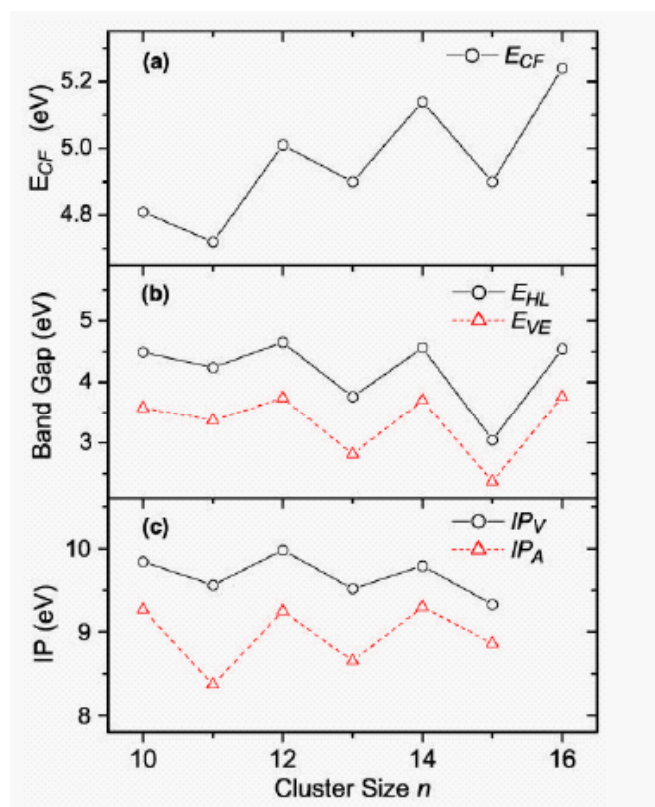


Figure 2. (Color) Electronic properties of $(\text{TiO}_2)_n$ clusters as a function of cluster size: (a) Cluster formation energies, (b) band gaps estimated from the HOMO-LUMO gap E_{HL} (using DFT with the B3LYP functional) and from the vertical excitation energy E_{VE} (using TDDFT with the B3LYP functional), and (c) vertical and adiabatic ionization potentials (IP_V and IP_A).