

Natural gas conversion from first principles

Frank Abild-Pedersen¹

¹Center for Atomic-scale Materials Design(CAMD), Department of Physics, NanoDTU,
Technical University of Denmark(DTU), 2800 Kgs. Lyngby, Denmark

*abild@fysik.dtu.dk

Introduction

The direct Gas-to-Liquid(GTL) conversion of methane into methanol is one of the most interesting reactions for which an effective catalyst needs to be identified.[1] The activation of the first C-H bond in methane, and the subsequent insertion of an oxygen atom or a hydroxyl group, constitutes a simple reaction scheme. However, the mechanism becomes very complicated due to other reaction products that are thermodynamically more favorable.

Materials and Methods

The electronic structure calculations are carried out using density functional theory [2,3] in a plane wave pseudopotential implementation [4,5] using the DACAPO code[6,7]. We use ultra-soft Vanderbilt pseudopotentials [8] to represent the ionic cores, which allows for a reasonable treatment of first-row atoms and transition metals with a relatively limited basis of plane waves. The plane wave cutoff in the calculations is 340 eV for the wave functions and 740 eV for the electron densities. Calculations on Fe, Co and Ni are spin polarized. The calculations are performed using the RPBE[6] exchange-correlation functionals on periodically repeated metal slabs. The model systems we use to represent the transition metal surfaces are 2x2 unit cells of the most close-packed surfaces and 1x2 unit cells for the stepped surfaces. The slab thickness is 3 layers in the most close-packed direction for all slabs. The uppermost close-packed layer is in all cases fully relaxed together with the adsorbed molecules using the quasi-Newton algorithm for finding a minimum. The geometry optimizations are considered converged when the forces are less than 0.05eV/Å. The lattice constant used for each metal is chosen as the calculated bulk lattice constant for the ground state structure using the RPBE functional. In the case of hcp metals the experimental c/a ratio is used. We use more than 10 Å of vacuum between the slabs, and the dipole interaction between the periodically repeated slabs is decoupled by the introduction of a dipole layer in the vacuum between the slabs [9,10]. A k-point sampling of 4x4x1 Monkhorst-Pack k-points [11] is chosen.

Results and Discussion

In this study we focus on obtaining a detailed understanding of the reaction energetics based entirely on Density Functional Theory. However, instead of exhaustively calculating adsorption energies and reaction rates for a large variety of different transition metals and alloys, we gain our insight by identifying the connections between adsorption energies, reaction barriers and the electronic structure of the metal or alloy in question. It has been firmly established that the complicated energetics involved in surface reactions can be correlated with the distribution of electrons in the metals[12-19] and that the localized d-electrons cause the observed differences between the different transition metals.[20,21] By building on these insights, we demonstrate that the complicated potential energy diagrams of the direct methane to methanol conversion can be determined with very few calculated

parameters. Furthermore, we show that this simple approach can be justified by arguments based entirely on the differences in the metal electronic structure.

Significance

It could be a useful tool for theoretical heterogeneous catalysis if one could predict transition state energies and how adsorption energies change over a series of metal surfaces as functional groups are added to a given adsorbed atomic species. This would facilitate a computational screening of catalytic surfaces not only for the methane to methanol reaction but also for many other complex reactions, without the necessity of performing the demanding detailed electronic structure calculations of every single involved adsorbate over the whole range of metals. Once in a position to reliably predict trends in adsorption energies of various intermediates, one could envision performing a first rough screening process based on the predictions alone. Subsequently, one could then focus the computational effort on those systems which were predicted to be near-optimal.

Acknowledgments

The author gratefully acknowledges contributions from J. Greeley, T. Bligaard, J. Rossmeisl, T. Munter, and J. K. Nørskov, CAMD, Technical University of Denmark, Kgs. Lyngby, Denmark.

References

1. G.J. Hutchings and S. H. Taylor, *Catal. Today* **49**, 105 (1999)
2. P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964)
3. W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965)
4. M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, J. D. Joannopoulos, *Rev. Mod. Phys.* **64**, 1045 (1992)
5. G. Kresse, J. Furthmüller, *Comp. Mat. Sci.* **6**, 15 (1996)
6. B. Hammer, L. B. Hansen, J. K. Nørskov, *Phys. Rev. B* **46**, 7413 (1999)
7. S.R. Bahn, K.W. Jacobsen, *Comp. in Sci. and Eng.* **4** (2002) 56
8. D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990)
9. J. Neugebauer and M. Scheffler, *Phys. Rev. B* **46**, 16067 (1992)
10. L. Bengtsson, *Phys. Rev. B* **59**, 12301 (1999)
11. H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976)
12. A. Eichler, F. Mittendorfer and J. Hafner, *Phys. Rev. B* **62**, 4744 (2000)
13. A. Roudgar and A. Gross, *Phys. Rev. B* **67**, 033409 (2003)
14. J. Greeley and M. Mavrikakis, *Nature Mater.* **3**, 810 (2004)
15. J. Greeley and M. Mavrikakis, *J. Phys. Chem. B* **109**, 3460 (2005)
16. F. Abild-Pedersen, J. Greeley and J. K. Nørskov, *Catal. Lett.* **105**, 9 (2005)
17. A. Michaelides, Z-P Liu, C. J. Zhang, A. Alavi, D. A. King and P. Hu, *JACS* **125**, 3704 (2003)
18. J. R. Kitchin, J. K. Nørskov, M. A. Barteau and J. G. Chen, *J. Chem. Phys.* **120**, 10 (2004)
19. Y. Xu, A. V. Ruban and M. Mavrikakis, *JACS* **126**, 4717 (2004)
20. B. Hammer and J. K. Nørskov, *Surf. Sci.* **343**, 211 (1995)
21. B. Hammer and J. K. Nørskov, *Nature* **376**, 238 (1995)