Modeling selective oxidation of hydrocarbons by V-based oxides

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Abstract: The economically viable conversion of alkanes to aldehydes or carboxylic acids would mark a substantial achievement for modern catalysis, making the supply of these important chemicals both less expensive and more environmentally friendly. V-based oxides show great promise as catalysts for these reactions, but at present do not have sufficient selectivity to be worthwhile. In this study, we examine these catalysts computationally, at an atomistic level, to rationalize their properties and their reactivity. Besides the geometric structure we study the electron distribution and the energies of hydrogenation and hydrolysis.
Keywords: VPO, $MoVO_x$, reducible oxide, oxidative dehydrogenation, computational catalysis.

1. Introduction

Selective oxidation reactions are of great importance to the chemical industry, allowing an almost direct transformation of alkanes and olefins to value-added chemicals such as aldehydes or carboxylic acids.[1,2] This talk addresses the modeling of structurally and electronically complex catalysts for such reactions, $MoVO_x$ and vanadium phosphate. $MoVO_x$, in particular the Mitsubishi M1 catalyst variant MoVTeNbO, is able to convert propane into acrylic acid with a selectivity of 61% and a conversion of 80%. The yield, however, is still unsatisfactorily low. Attempts to modify the structure to improve the selectivity are currently hampered by the poorly-defined understanding of the active site. Numerous metal sites in the structure have fractional occupancies, and even amongst those with known occupancy, multiple oxidation states may be present. We carried out a density functional theory exploration of the $MoVO_x$ catalyst, exploring a number of factors that affect reactivity, specifically the distribution of reduced centers, as well as the propensity of this material for carrying out hydrogenation and hydrolysis. The results are compared to those we determined for VPO systems. The latter catalyst material, whilst complex in many regards, is somewhat simpler as only one type of metal is present.

2. Theoretical

Modeling $MoVO_x$ by itself is already a notable challenge in computational catalysis as the work horse, GGA-DFT, fails to provide a reliable description of the material. We present efforts to arrive at adequate models for demonstrating that the electronic structure of the $MoVO_x$ catalyst material plays an important role for the reactivity. Periodic bulk and slab models of between 1 and 4 layers were used. Calculations were carried out with Crystal 14 (using the B3LYP exchange correlation functional) or VASP, with PBE+U, U(V) = 2.3 eV and U(Mo) = 8.6 eV.[3,4] In addition to the periodic models, two cluster models with metal centers were invoked for studying the accuracy and the localization of reducing electrons, using Turbomole, employing functionals the M06, B3-LYP, PBE0, TPSSh, PBE, and M06-L and the aug-cc-pVTZ basis set.

3. Results and discussion

In heterogeneous catalysis, finding an appropriate model for the active site often constitutes the most sizeable challenge to computational modeling. This task is much more difficult for reducible oxides as standard GGA-DFT fails and rather large cluster models have to be employed. Besides geometric effects, we have to understand the electronic structure to be modeled to capture the essentials of a cluster model. To explore which amount of single-determinant exchange to a standard GGA is beneficial, we carried out test calculations on oxidic 1 and 2 metal center complexes and compared them against a CCSD(T) reference.[5] The B3LYP functional produced the smallest deviations, with less than 20 kJ mol^{-1} overall mean absolute deviation to the CCSD(T) results. Consequently, we used in the following predominantly B3LYP and cluster models or CRYSTAL calculations where B3LYP is affordable.

For modeling the oxidation of propane on $MoVO_x$, we considered the likely distribution of reduced centers within the material. By changing the distribution of such electrons, subtle changes in the local geometry are instigated. Already this simpler material in its ideal structure provides 60 possibilities of how to distribute V^{4+} centers amidst the V^{5+} atoms. Controlling the distribution of reduced centers may be crucial because many variations should be energetically accessible, with a total range of up to ~100 kJ mol^{-1}. This could very well have a larger impact on the chemistry at such surfaces. We studied dehydrogenation and hydrolysis at the surface, and the surface sites most amenable to these model reactions. The wide distribution of reduced centers is particularly pronounced during these reactions; we observe that during hydrogenation, it is vanadium centers of a sub-surface layer that are ultimately reduced, leading to a gain in energy of 65–95 kJ mol^{-1}. In contrast, we did not find any dependency of the energetics of hydrolysis on the reduced centers. However the energy for hydrolysis is also highly site-dependent, with a preference of 30 kJ mol^{-1} towards adding an OH moiety to molybdenum. Finally, we report the oxidation of butane on VPO, using CH_4 as a model for longer hydrocarbon chains, at various surfaces. Experiment has shown oxidation-dependent catalytic activity, which we explore by mapping the adsorption energy of hydrogen to the barrier of C-H cleavage. We determined that this barrier is a function of oxidation state, with increased reactivity when the 3+ oxidation state of vanadium is formed as final state.
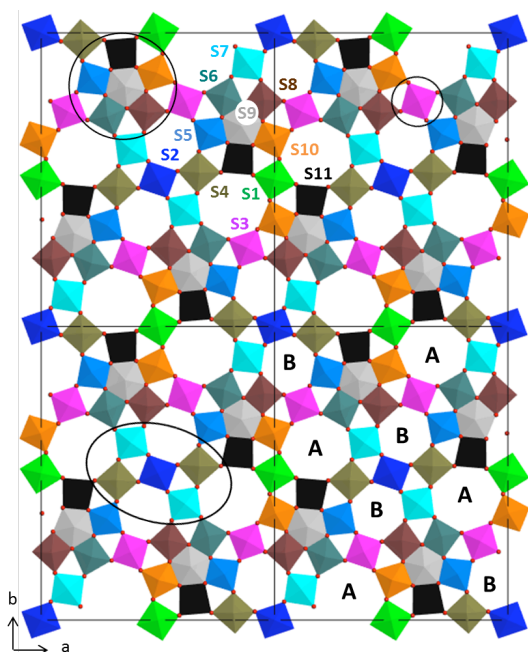

Figure 1. Unit cell of the $MoVO_x$ material. S1 to S11 denote the metal sites, A and B label the heptagonal and hexagonal channels, respectively. The pentameric and pentagonal units, two structural motifs believed to be of particular importance, are circled.

4. Conclusions

Without a reliable understanding of the electronic structure, insight into the chemistry at such catalysts is a challenge. In addition to information about active sites, understanding the distribution of reduced centers and its flexibility is important before exploring the catalytic mechanism of these systems. Unraveling the effect of the reduced centers on the reactivity offers a promising avenue to understanding why these materials can catalyze such complex transformations. Unfortunately a much larger body of research is necessary to better understand the effects of the electronic structure on the reactivity until we finally reach an atomistic understanding.

References
1. J. Grant, J. Venegas, W. McDermott, I. Hermans, Chem. Rev. (2017), DOI: 10.1021/acs.chemrev.7b00236.
2. C.-C.Chiu, T. Vogt, L. Zhao, A. Genest, N. Rösch, Dalton Trans. 44 (2015) 13778.
3. S.L. Dudarev, G.A. Botton, S.Y. Savrasov, C.J. Humphreys, A.P. Sutton, Phys Rev B 57 (1998) 1505.
4. S. Lutfalla, V. Shapovalov, A.T. Bell, J Chem Theory Comput 7 (2011) 2218.
5. S. Dinda, C.-c. Chiu, A. Genest, N. Rösch, Comput. Theor. Chem. 1101 (2017) 36.