

Effective approach to theoretical investigations of heterogeneous catalytic processes on metal oxides

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Heterogeneous catalysis is widely used in various important industrial processes. Nevertheless, mechanisms of these processes are poorly understood due to lack of effective investigation approaches. Any experimental technique by itself is insufficient for unquestionable determination of mechanism, it has to be combined with thorough theoretical study. In its turn, simulation of crystal surfaces is one of the most challenging problems in computational chemistry. Use of periodic models for these purposes gives rather accurate results but still remains extremely expensive (regarding CPU time); in addition it is difficult to treat charged systems in terms of this approach. Another way is to use cluster models which are cheaper but less accurate. Moreover, there is a problem of reasonable calculation of vibrational frequencies (for locating transition states).

To solve these problems we have developed a new approach for surface calculations based on three-layers embedded cluster models. To obtain such a model one should choose appropriate number of metal atoms that are able to represent the adsorption center and to include them together with all oxygen atoms of their coordination spheres into the first layer. This layer is treated explicitly using large basis set. All metal atoms that are connected with oxygen atoms from the first layer form the second layer of “soft” charges which are described only with effective core potential. The third layer is an array of point charges that are located at the positions of corresponding atoms in the crystal structure of the oxide. This layer can be enlarged without loss of calculations efficiency, because only the resulting background charge distribution is included into the Hamiltonian. Obtained cluster model as a whole should be neutral. The array of point charges takes into account differences in electron density distribution between bulk crystal and cluster. The layer of “soft” charges plays role of a buffer which prevents excessive polarization of the model and its folding. Coordinates of the second and third layers are kept frozen during the optimization. While calculating vibrational frequencies, removing of normal modes that involve contribution of the “soft” charges allows using automatic procedure of transition states optimizations implemented in such programs as Gaussian.

The proposed approach has been tested by calculating methane activation barrier on γ -Al₂O₃ [1] and by studying NO reduction process on Ag/ γ -Al₂O₃ [2]. Thus, accuracy of our approach is not inferior to that of periodic calculations.

References

- [1] M.C. Cholewinski et al. ACS Omega (2018) 3(12): 18242
- [2] Vit. E. Matulis et al. J. Ph. Chem. C (2021) 125: 419