

Accounting for entropy in reactor-level simulations of ethylene epoxidation: does it really matter?

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Highlights

- Ethylene epoxidation on silver is explained using first-principles simulations.
- Entropy is not accounted in DFT simulations but added in post-processing.
- Different methods of entropy calculations influence the reaction rate and selectivity.
- Complete potential energy sampling outperforms simpler methods.

1. Introduction

Ethylene epoxidation is an important selective oxidation, which is industrially used to produce ethylene epoxide in millions of tones yearly. [1] Silver has been recognized as the most suitable catalyst, which remains unsurpassed despite extensive research. First-principles modelling of the reaction has revealed the reaction mechanism and what influence different dopants and defects. An often-neglected contribution to the overall kinetics is the entropy, which is usually described by the conventional harmonic approximation without additional thoughts. In this work, we consider the effect of four different approaches to the calculation of entropy for ethylene epoxidation on silver: harmonic approximation, free translator, hindered translator and complete potential energy sampling. [2,3]

2. Methods

The calculations were performed with VASP, using the plane-wave formalism. The catalyst was modelled as a four-layer slab of Ag(111) in a 4x4 supercell. The bottom two layers were kept fixed in their bulk positions. Dipole corrections and van der Waals interactions were included, as is customary. A full reaction mechanism was modelled [3], including the adsorption of reactants and all elementary steps. The transition states were located using the dimer method with the force threshold of 0.01 eV/Å. Using the Eyring equation, which included the entropic contribution, we computed the reaction rate constants for each of the four scenarios (modelling entropy as the harmonic approximation, free translator, hindered translator and complete potential energy sampling). The kinetic constants were cast in a microkinetic model, which described a realistic plug-flow reactor including mass transfer and diffusion. [5]

3. Results and discussion

On Ag(111) without dopants or defects, the selectivity towards ethylene epoxide is below 50 % in the conventional harmonic approximation. However, the entropy is significantly underestimated when the harmonic approximation is used. The free translator approximation is shown to overestimate the entropy but the hindered translator and CPES (complete potential energy sampling) provide the most realistic values for entropy.

CPES is a computationally costly method and is only realistically useful for simple adsorbates, such as single atoms. More complex adsorbates, such as oxametallocycles or multi-atom transition states can not be efficiently evaluated over the entire surface. We show, however, that the hindered translator, which is computationally much cheaper, performs similarly well. Both approaches yield comparable results to the experiment.

In addition to influencing the absolute rate of the reaction, different approaches to modelling entropy also affect the selectivity. This is because they influence different elementary reaction steps in a different fashion, changing the ratio of the products in the process.

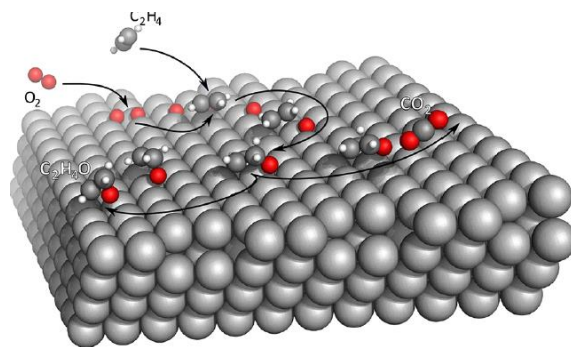


Figure 1. The reaction mechanism used in the study.

4. Conclusions

We observe that despite small absolute differences in the Gibbs free energy due to a different description of entropy, the effects on the overall performance of the reactor, the turn-over frequencies and selectivities are large. This is attributed to the exponential relation between the kinetic rate constants and the Gibbs free energies.

The complete potential energy sampling gives the most accurate results, but its computational cost is too high to be useful practically. Instead, a hindered translator or free translator provide a sufficiently accurate description, depending on the adsorption interaction of the adsorbate. Harmonic approximation is notorious to underestimate the entropy and, despite being most commonly used, performs worst.

References

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Keywords

Ethylene epoxidation; DFT; entropy, kinetic modelling.