# Exploring the Migration and Clustering of Catalytic Relevant Defect Sites via First-Principles-Based kMC Simulations

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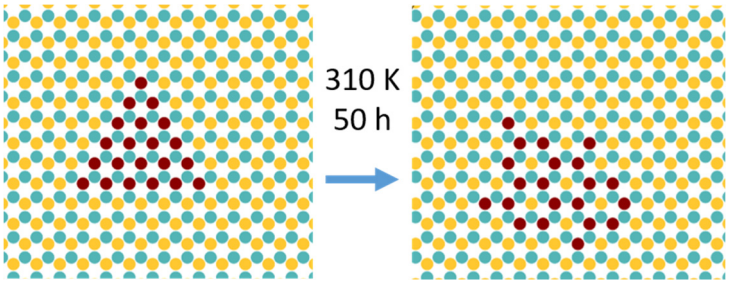
A rising concept in the field of catalysis is the idea of "defect engineering,"[1] which introduces defects into a catalyst structure to tune the activity and selectivity. From this, it can be seen that defect and vacancy sites are important for catalysis. For instance, the S-vacancy sites on $MoS_2$ have recently been discussed as essential for the catalytic $CO_2$ conversion.[2,3] It is also known that the electronic structure of such S-vacancies, and with that likely also their catalytic behavior, can vary with their sizes and shapes.[4] Thus, whether an introduced defect structure on a catalyst is stable or not becomes a critical aspect when evaluating the long-term applicability of a catalyst.

In the context of computational investigations on $MoS_2$, literature has, so far, only reported the migration barriers of S-vacancies in different environments.[5] However, what these data mean for long-term stability and how they are reflected in the surface structure of a defective $MoS_2$ surface has remained unclear. This presentation will show how we combine DFT calculations with a kinetic Monte Carlo model to investigate these issues.[6] On the one hand, we will discuss the stability and surface mobility of S-vacancies of different sizes and shapes. On the other hand, it will be shown how defective $MoS_2$ surfaces evolve with time. It could be shown that S-vacancy sites on $MoS_2$ are highly dynamic structures that are constantly changing their shapes. However, the mobility of the S-vacancies is typically limited to a constrained space, so migrations over large distances are rather unlikely. This is a direct result of the strong dependency of the vacancy migration barriers on the immediate surrounding of the vacancy site.




Using our kMC model we show that large, extended S-vacancies are relatively unstable on $MoS_2$. In equilibrium, one finds an alternating pattern of occupied S-sites and S-vacancies instead. The results shown in the presentation will contribute to a better

understanding of catalyst aging and deactivation processes. In addition, it will be illustrated that it is vital to consider the stability of defect structures when designing "defect-engineered" catalysts.

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