

# Combined DFT and Kinetic Monte Carlo Studies of Formic Acid Decomposition on Au<sub>18</sub> Nanoclusters

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Formic acid (FA) is a promising non-toxic, organic hydrogen (H<sub>2</sub>) storage material (4.4 wt. % H<sub>2</sub>). Being an abundant byproduct when producing levulinic acid from biomass, it has been envisioned as an *in situ* H<sub>2</sub> source for converting levulinic acid to  $\gamma$ -valerolactone, which is a valuable precursor for production of various fuels and chemicals.<sup>2</sup> Additionally, it may also be utilized in fuel cells, e.g. in the direct formic acid fuel cell.<sup>3</sup> To unlock its potential however, we need to find ways to quickly and selectively release the stored hydrogen from FA. Using Au/SiC catalysts, Mavrikakis and co-workers showed experimentally that FA decomposition activity increases with decreasing Au particle size.<sup>4</sup> Based on detailed Density Functional Theory (DFT) calculations, they concluded that extended Au(111)/(211)/(100) surfaces were not the active sites for the reaction, and that sub-nanometer Au clusters with highly undercoordinated sites were likely to be responsible for FA decomposition activity.<sup>4</sup> Based on these findings, we calculated potential energy surfaces for FA decomposition on Au<sub>n</sub> (n=3–25) clusters using DFT. It was found that Au<sub>18</sub> had a potential energy profile that could best reproduce the experimental results when placed in a microkinetic model (MKM), and thus likely contains the active site for the reaction.

In this work, we further probe the activity of Au<sub>18</sub> clusters by performing comprehensive Kinetic Monte Carlo (KMC) simulations with our DFT results. KMC simulations outrank mean-field models in terms of fidelity, by being able to capture spatial inhomogeneities in the site distribution of Au<sub>18</sub>, as well as correlations due to adsorbate ordering. We indeed noticed strong adsorbate-adsorbate interactions for this system. To factor in their effects on the reaction energetics, we employ a cluster expansion, parameterizing the interaction energies of adsorbates in terms of point and multi-body interactions.<sup>5</sup>

Our simulations reveal that the TOF of H<sub>2</sub> on Au<sub>18</sub> is much closer to the experimental TOF compared to extended Au(211)/(100) surfaces,<sup>4</sup> and is thus a likely model of the active site for FA decomposition. A triangular ensemble of three Au atoms, each with a coordination number of five (CN=5 sites), is found to be the active site. Our work will offer valuable insights into the molecular pathways of FA decomposition, and serve to guide future efforts to optimize the shape and size of Au catalysts for the FA decomposition reaction.

## References

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