

Reactive force field optimization and MnFeO₃ catalyst theoretical investigation

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Introduction and background

Motivation: to remove VOCs from the environment

Method: perform reactions to degrade complex organic compounds to CO₂ and H₂O

Economy/Feasibility (time, energetics): use catalysts to speed up/enable reactions

More economy: use less expensive and readily available catalysts Pt, Au → Fe, Ni, Cu, Mn

In a recent research (in) catalytic activity of several MnMO_x (M=Cu,Fe,Ni) catalysts the Reactive force field (ReaxFF) method has been shown to model well such processes. The investigation raised interest in developing parameters for calculation of mixed metal-oxide species, which were at the time non-existent. Here we present first and preliminary results of training the ReaxFF for the Mn-Fe-O-C interaction.

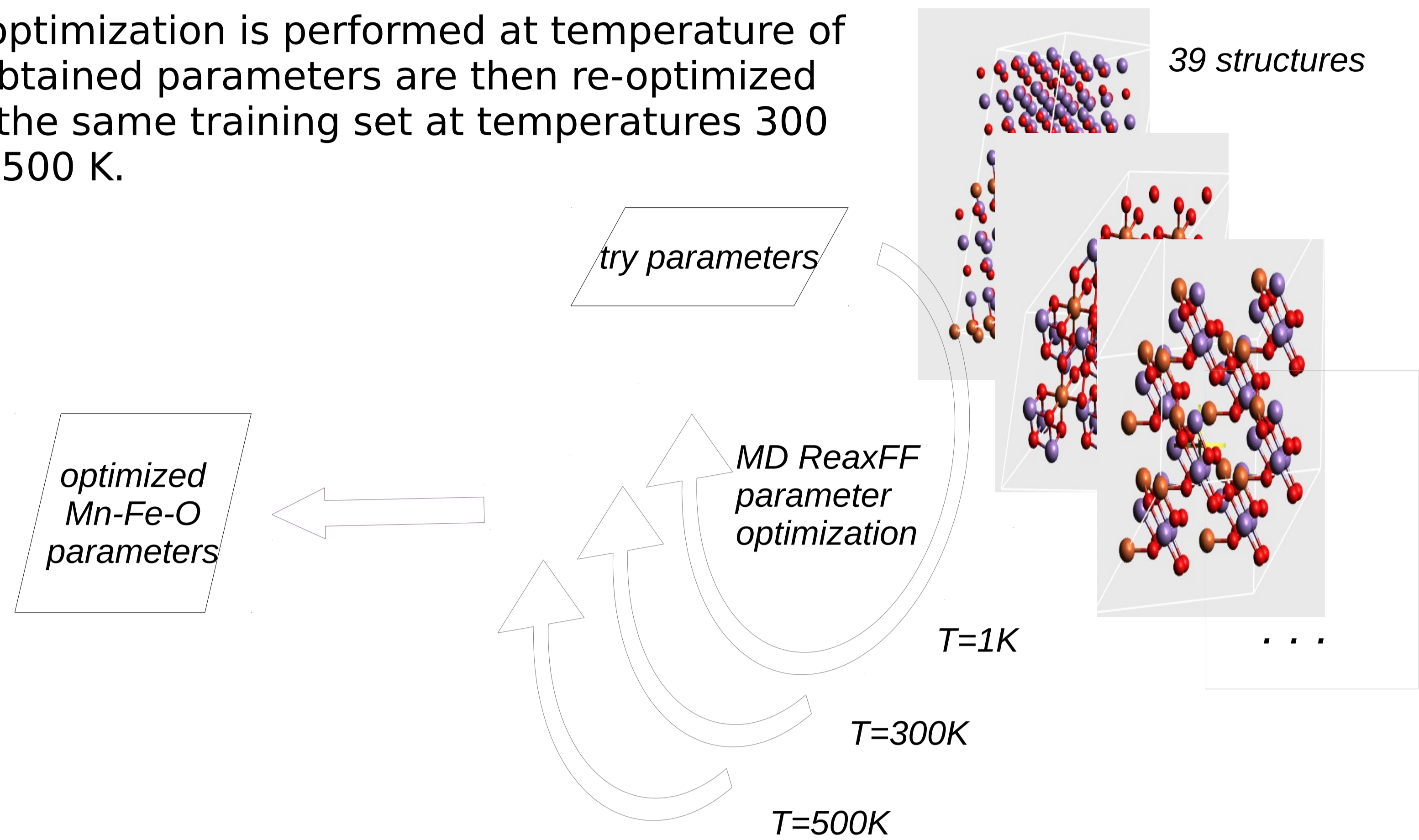
Methods

The training set of 39 structures consisting of at minimum the Mn, Fe and O atoms, obtained in their crystal form from Materials Project database [1]. Each step in parameter optimization has been done performing MD minimization of 5000 steps of 0.1 fs using the NVT/Berendsen thermostat. The optimization of the parameters has been done using the parabolic search as implemented in the original van Duin code [2] with small in-home modifications to the code.

Insert: Training set

Mn₄FeO₅ Mn₂FeO₄ Mn₃FeO₈ Mn₂FeO₃
 Mn₁₇Fe₁₃O₄₀ Mn₉FeO₁₀ Mn₄FeO₈ Mn₅FeO₁₂
 Mn₅(FeO₃)₄ Mn₁₃Fe₃O₃₂ Mn₅(FeO₃)₄ MnFe₂O₃
 Mn₂FeO₄ Mn₂FeO₆ MnFeO₃ Mn(FeO₂)₂ Mn₃FeO₈
 Mn₅Fe₃O₁₆ MnFe₄O₅ Mn(FeO₂)₂ Mn₁₃Fe₁₁O₃₂
 MnFeO₄ Mn₉(FeO₆)₄ Mn₇Fe₃O₂₀ Mn₃Fe₃O₈
 Mn₃FeO₈ MnFeO₂ MnFe₅O₈ Mn₅FeO₁₂ MnFeO₄
 Mn₃FeO₈ MnFeO₃ MnFe₂O₃ Mn₂₃FeO₃₂
 Mn(FeO₂)₂ Mn₃Fe₅O₁₂ Mn₂FeO₆ Mn₂FeO₆
 Mn₁₉Fe₁₇O₄₈

First, optimization is performed at temperature of 1 K. Obtained parameters are then re-optimized using the same training set at temperatures 300 K and 500 K.



Results

The force field is applied to the process of toluene adsorption / degradation on MnFeO₃ catalyst: 100000 steps of 0.25 fs MD calculation using NVT/Berendsen thermostat at 500 K of a MnFeO₃ crystal slab to which a 30 Å vacuum layer with 6 toluene molecules was added.

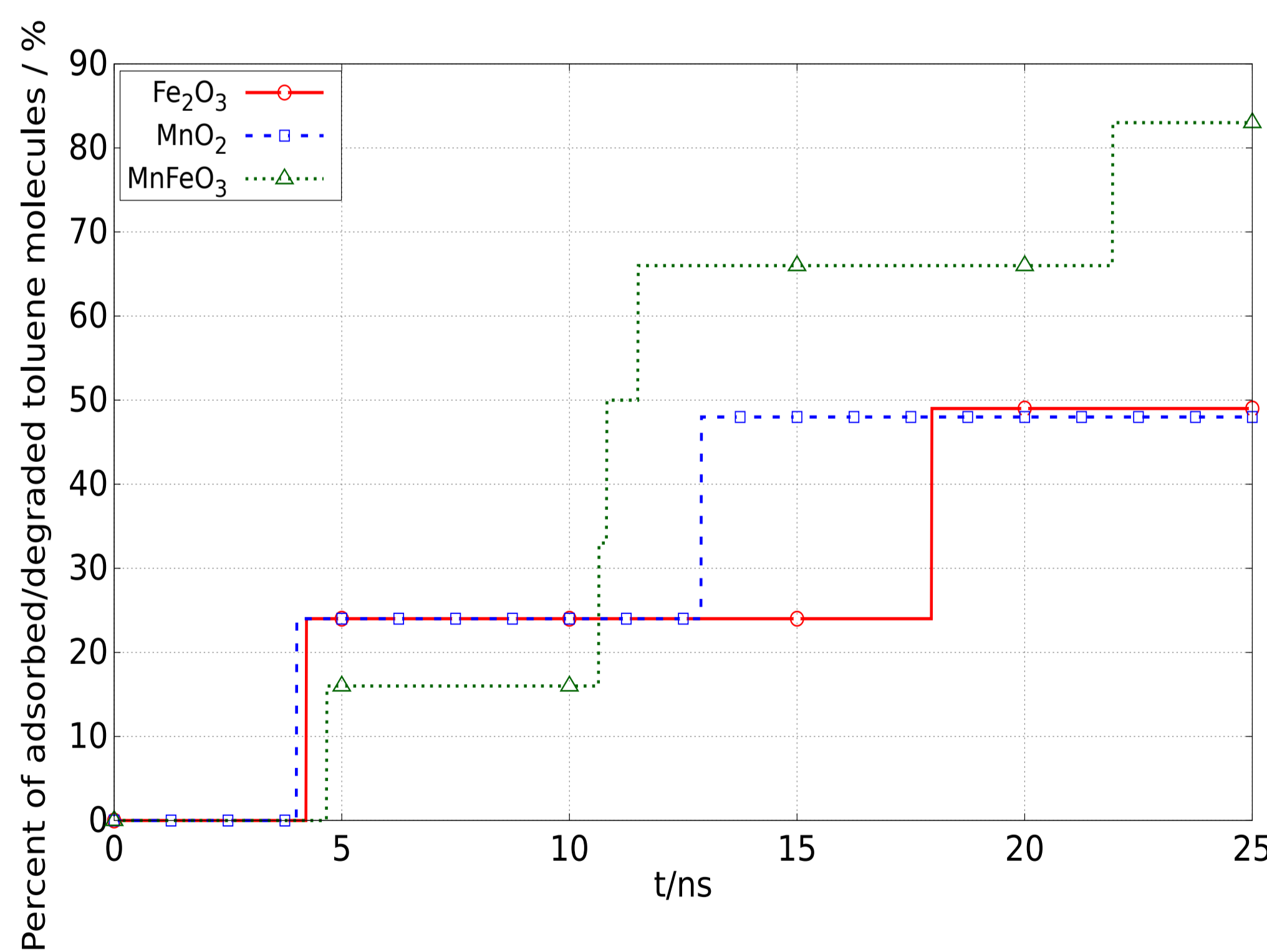
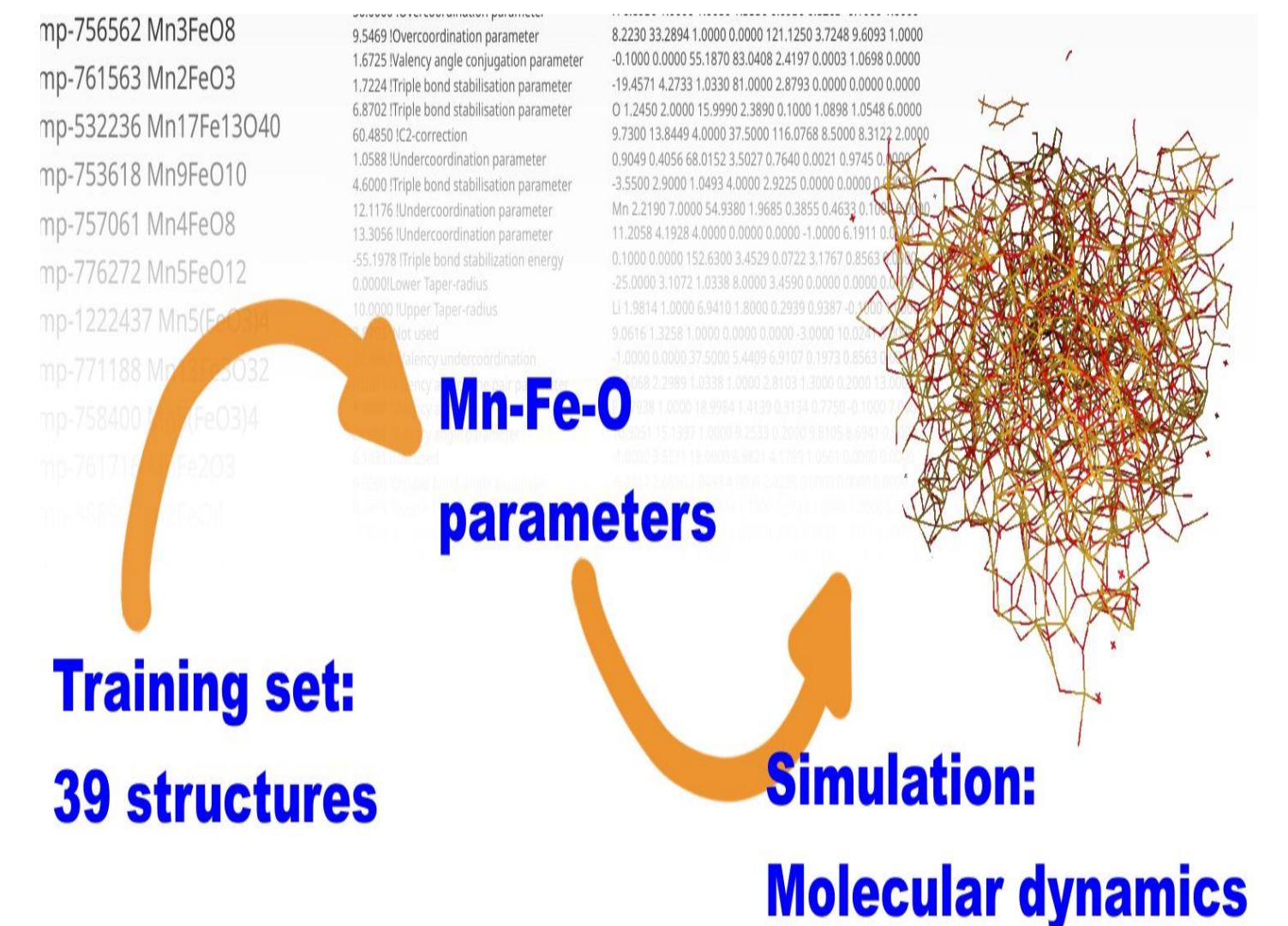
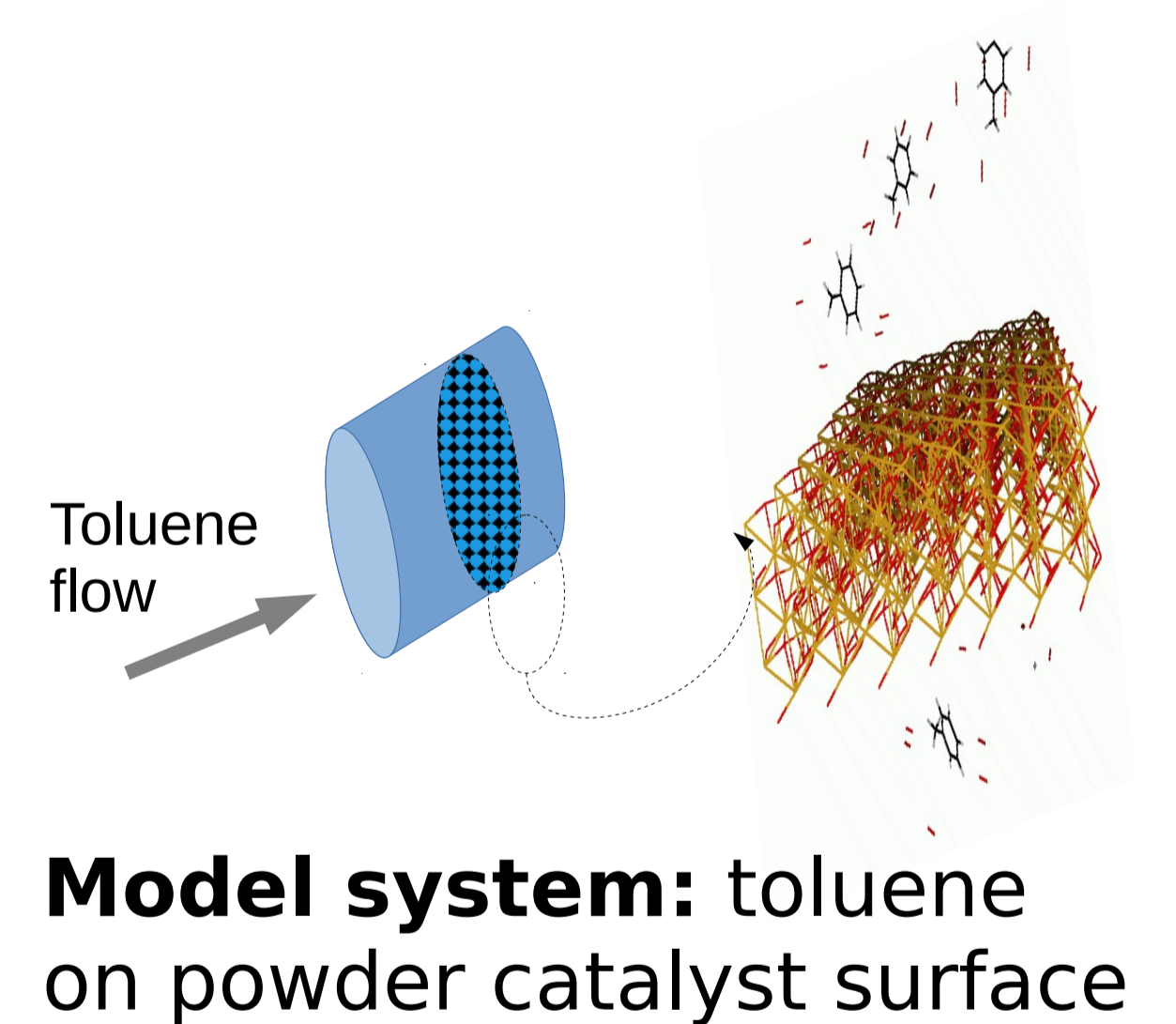


Figure: Comparison of predisposition of activity for toluene removal: 25ns ReaxFF simulation for Fe₂O₃, MnO₂ and MnFeO₃ at 500K.



Conclusions

- ReaxFF calculations using optimized parameters obtained here show agreement with experimental expectations
- Some caution is advised, since the parameters were not optimized to predict crystal structure changes when Mn content changes in Mn_{1-x}Fe_xO₃

Acknowledgement

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References

- [1] A. Jain et al., *APL Materials*, 1(1) (2013) 011002.; S. P. Ong et al., *Comp. Mat. Sci.* 68 (2013) 314–319.
- [2] A. C. T. van Duin et al., *J. Phys. Chem. A*, 105 (2001) 9396–9409.