

Toluene oxidation on metal-oxide catalysts: Theoretical modeling

Vjeran Gomzi

University of Zagreb, Faculty of electrical engineering
and computing, Zagreb, Croatia

vjeran.gomzi@fer.hr

Introduction

Reactive organic species are often removed from the environment by reactions involving catalytic centers. The criteria in choosing a catalyst are its activity for specific reaction and the material availability and the cost of production. A set of relatively inexpensive potential catalysts for toluene degradation is obtained by mixing Mn with other metal atoms, like Fe, Ni, Cu in oxygen atmosphere. Only the most abundant oxide species in each mixed metal-oxide mixtures is theoretically investigated here.

Methods

The repeated unit cell has been formed for Mn_2O_3 , Fe_2O_3 , NiO, CuO and MnO_2 slab consisting of approximately 1000 atoms from crystal surrounded by approximately 30 Å vacuum layer to which several toluene and oxygen molecules were added.

For calculation, the in-home compiled software based on the reactive force-field method was used as implemented in the ReaxFF code developed by Duin et al. [1].

The temperature controlled Berendsen thermostat (NVT) with a damping constant of 0.1 fs is used for 2.5 fs molecular dynamics (MD) calculation on the initially energy-minimized crystal structure at 500 K. Toluene is then added and additional 25 ns MD calculation is performed (100000 steps of 0.25 fs) at 500 K using the force fields available for the respective structures.

Additionally, calculations involving temperature rise from 500K to 700K, followed by 6.25 fs calculation at 700K and temperature drop back to 500K were performed. These were done in an attempt to model the much longer time available for reactions under experimental conditions more realistically.

[1] van Duin, A. C. T., Dasgupta, S., Lorant, F. & Goddard, W. a. ReaxFF: A Reactive Force Field for Hydrocarbons. *J. Phys. Chem. A* 105, 9396–9409 (2001).

[2] G.K. Boreskov, Catalytic activation of dioxygen, in: J.R. Anderson, M. Boudart (Eds.), *Catal. Sci. Technol.* Vol. 3, Springer-Verlag Berlin and Heidelberg GmbH & Co. KG, Berlin, 1983: pp. 39–137.

Results

Binding and/or toluene reactions are summarized in Fig. 1, where the net amount of free toluene molecules is shown as a function of simulation time (left y-axis, green). Based on the results of the simulations, toluene is progressively bound/adsorbed without significant desorption only on Fe_2O_3 and MnO_2 surfaces. This behavior seems not to be significantly modified upon the crystal plane surface change, as verified by taking at least two crystal plane simulations for Fe_2O_3 and Mn_2O_3 crystals (data not shown here). Upon short heating period, for these two oxides toluene adsorption increases (Fig. 1, blue).

Based on theoretical simulations, predisposition for good catalytic activity was estimated according to the maximum relative number of adsorbed toluene molecules during the simulation interval (not necessarily at the end). Comparison of the catalytic activity and estimated values for both toluene and oxygen adsorption is given in Table I. Binding energies and theoretically predicted catalytic activity of single oxide catalysts is related for all three oxide species predicted to bind toluene (Fe_2O_3 , MnO_2 and NiO): the higher the binding energy, the better the predicted catalytic behavior. Furthermore, if the oxygen binding energies on surface of these oxide species as found by Boreskov in [2] are compared to the respective predicted catalytic activity, we see that the largest values are for the most active species in predicted toluene removal (see column 3 in Table I).

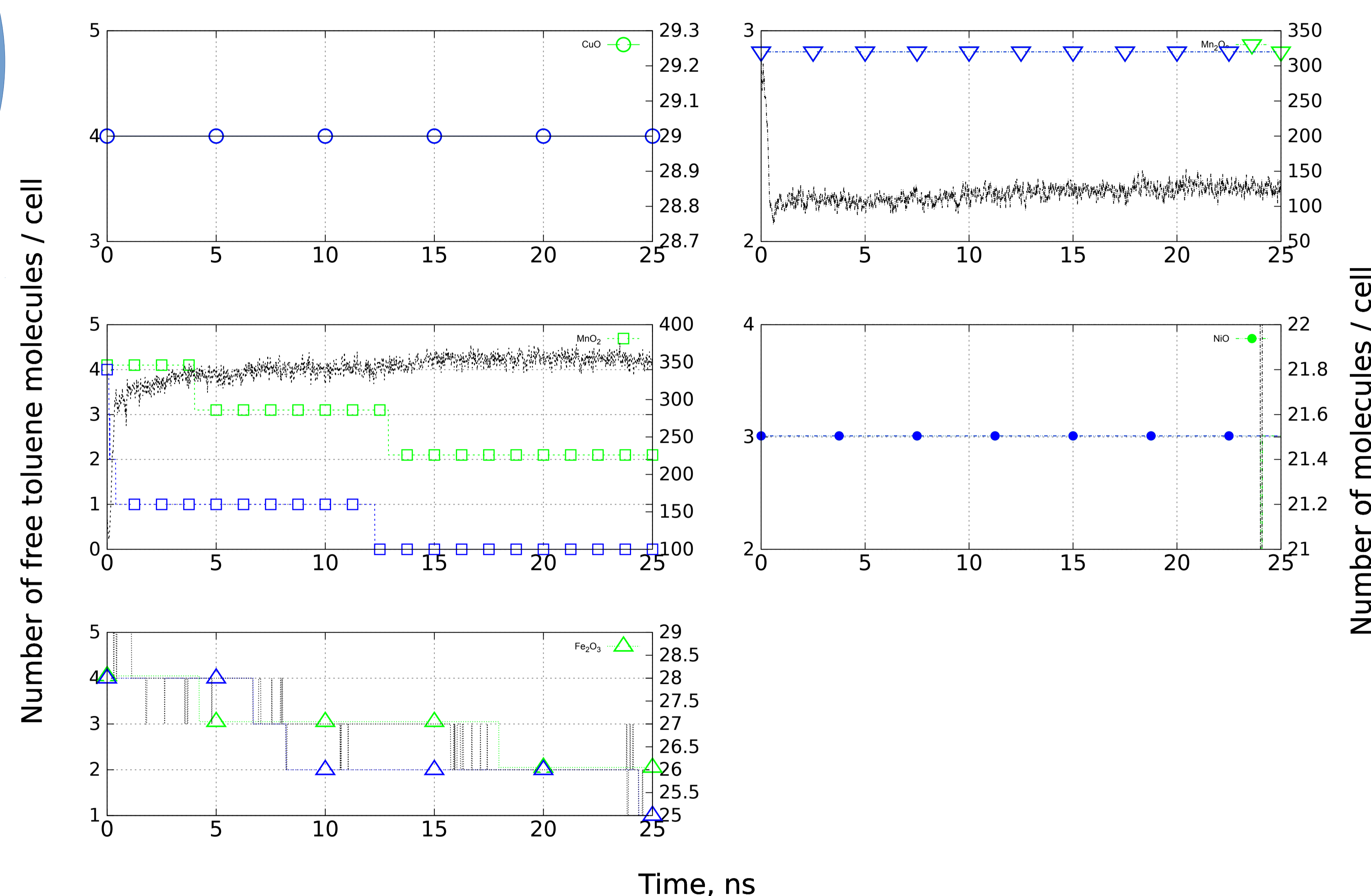


Figure 1. Number of free (unbound) toluene molecules as a function of the simulation time. (green – 500K, blue – T rise to 700K). For CuO, Fe_2O_3 and MnO_2 four toluene molecules were initially added, while for simulation of Mn_2O_3 and NiO, there were three free toluene molecules initially. Right y-axis (and black plots) show variation of total molecular fragments number during simulation.

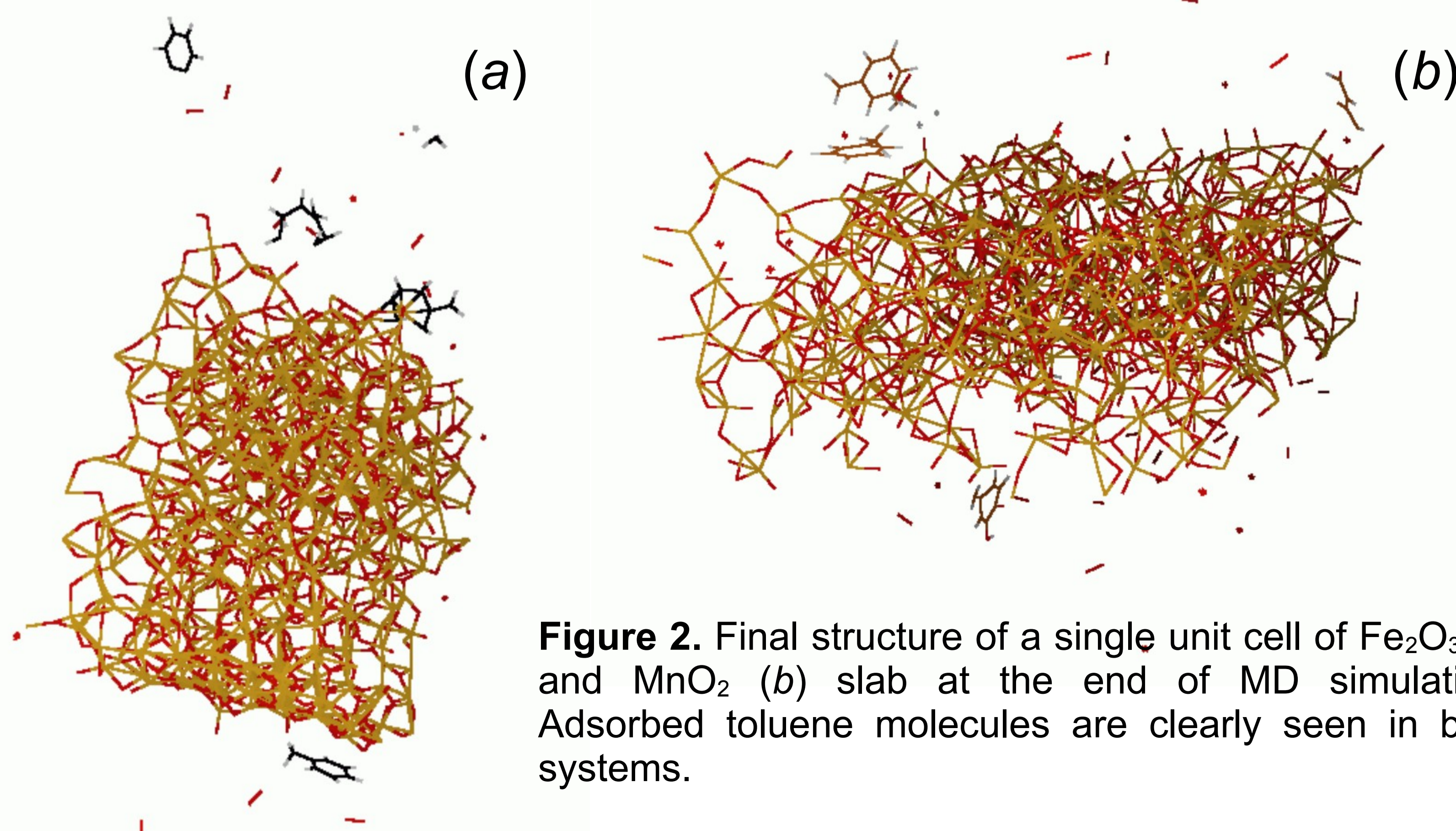


Figure 2. Final structure of a single unit cell of Fe_2O_3 (a) and MnO_2 (b) slab at the end of MD simulation. Adsorbed toluene molecules are clearly seen in both systems.

Table I. Toluene adsorption on single crystal surfaces.

	Toluene adsorption energy kJ/mol	Catalytic activity %	O ₂ adsorption energy ** kJ/mol
Fe_2O_3	251-1675	50	142
Mn_2O_3	-	0	-
NiO	84-251	33	79
CuO	-	0	75
MnO_2	<251	50	84

* See explanation and definition in the text.

** Taken from Boreskov [2].

Conclusions

According to theoretical simulations, MnO_2 and Fe_2O_3 have great potential for toluene adsorption. This finding is consistent with the experimentally observed best catalytic activity of MnFeO_x which consists predominantly of the same two metal oxides. Based on the results presented in this study, it can be concluded that theoretical study of toluene interaction on the surface of the single metal oxides in the oxygen atmosphere using the ReaxFF reactive force field can be successfully used for the prediction of activities of the manganese-based mixed oxides for toluene oxidation