

Modeling Generation and Growth of Iron Oxide Nanoparticles from Representative Precursors through ReaxFF Molecular Dynamics

Electronic Supplementary Information (ESI)

*Giovanni Barcaro^{*a} and Susanna Monti^b*

^aCNR-IPCF, Institute of Chemical and Physical Processes and ^bCNR-ICCOM, Institute of
Chemistry of Organometallic Compounds, via G. Moruzzi 1, I-56124 Pisa, Italy

E-mail: giovanni.barcaro@pi.ipcf.cnr.it

Figure S0 depicts the **initial configuration** of the cubic simulation box (side 90 Angstrom) created to describe the case with $N=2$, $L=6$. The box contains an $L \times L \times L$ array of $\text{Fe}(\text{COOR}_N)_3$ precursors.

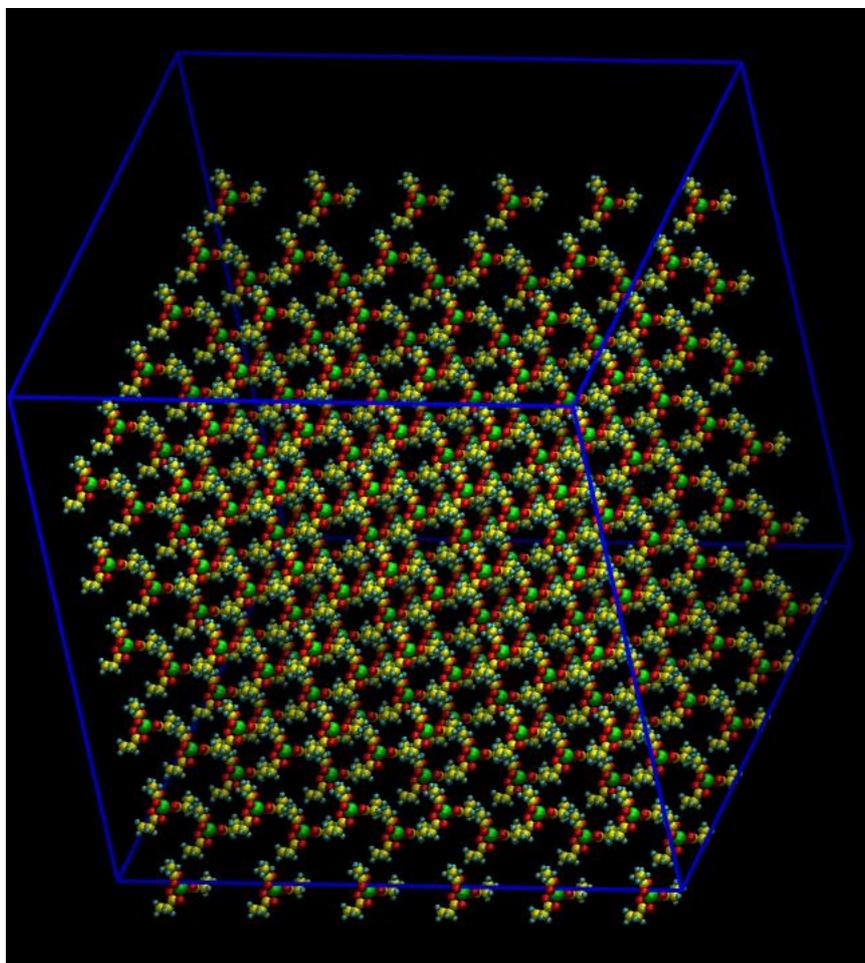


Figure S0. Initial configuration of a simulation box (side 90 Angstrom) containing an $L \times L \times L$ array of $\text{Fe}(\text{COOR}_N)_3$ precursors ($N=2$, $L=6$). Iron, oxygen, carbon, and hydrogen atoms are represented by green, red, yellow, and cyan balls, respectively.

In order to check the validity of the model in **presence of solvent molecules**, we performed a simulation by employing the following conditions: $N=2$, $L=6$ and $p_0=0.85$ at a temperature of $T=300$ K. In absence of explicit solvent molecules, these conditions are those presenting the fastest rate of NP growth. When adding explicitly solvent species, specifically 1080 molecules of dibenzylether (a commonly used solvent used in the synthesis of FeOxNPs, see Ref. 19 of main text) were added to the simulation box, similar qualitative results were obtained at the expense of a slightly slower reduction in the number of residues and in the creation of modified oxygen atoms, see Figure S1.

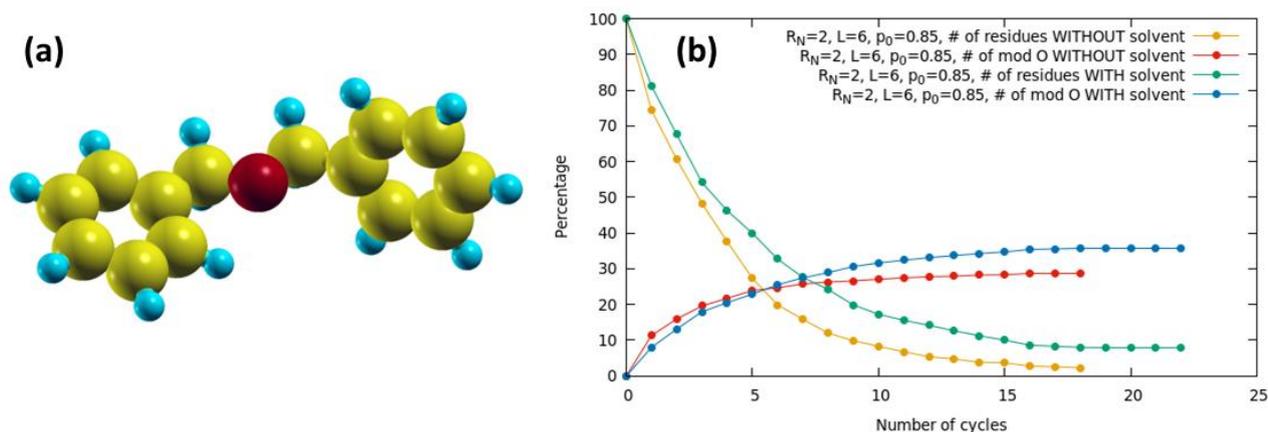


Figure S1. (a) Structure of the dibenzylether molecule; (b) percentage of residues and modified oxygens (bridge + radicals) when $N=2$, $L=6$ and $p_0=0.85$ at a temperature of $T=300$ K in absence (yellow and red lines) and in presence (green and blue lines) of solvent molecules inside the simulation box. Oxygen, carbon, and hydrogen atoms are represented by red, yellow, and cyan balls, respectively.

The cut-off distance 2.75 Angstrom used to calculate Iron Coordination (IC) in Step 2 of the growth protocol has been chosen on the basis of a typical **Fe-O pair radial distribution function** in reactive coils, as shown in Figure S2. The value of 2.75 Angstrom corresponds to the minimum of $g(r)$ after the wide peak corresponding to the first shell of Oxygen atoms around Fe atoms.

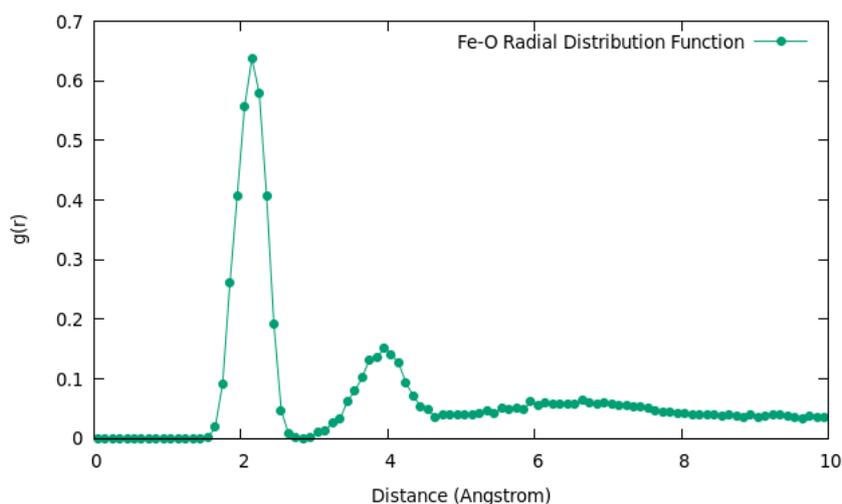


Figure S2. Typical Fe-O radial pair distribution function in a reactive coil.

Oxygen atoms in the residues can undergo different **treatments**, according to their **IC** (Iron Coordination). Figure S3 depicts 3 typical situations (extracted from real growth runs) describing cases b) to d) of step 2 of the growth protocol (see main text).

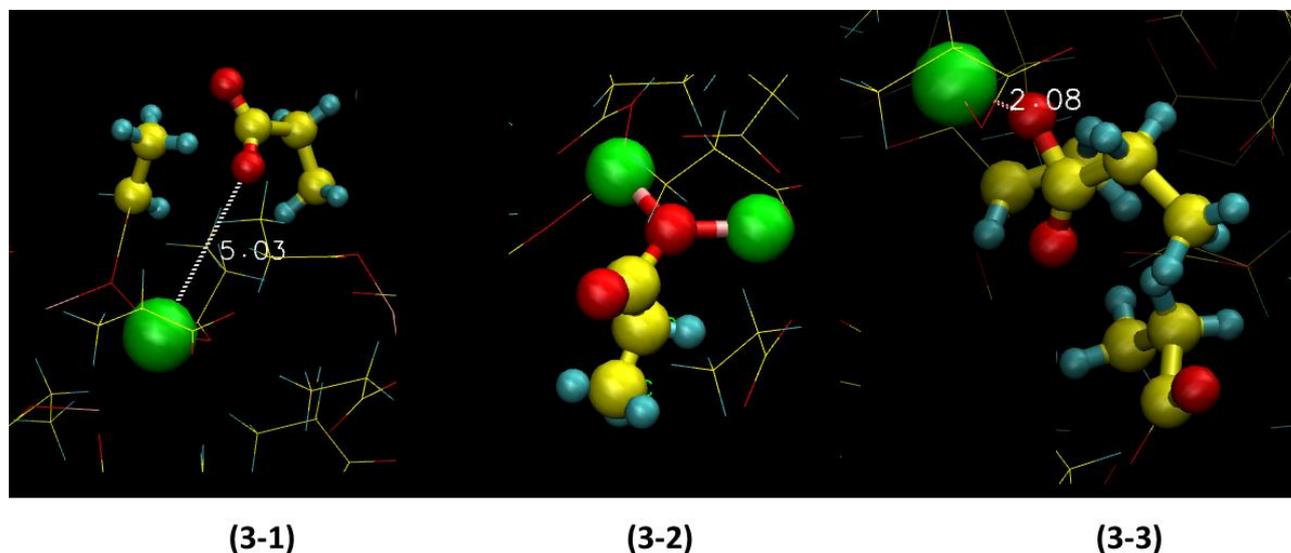


Figure S3. (3-1) Residue in which $IC(O1)=IC(O2)=0$, hence the residue is removed from the simulation box; (3-2) residue in which $IC(O1)=2$ and $IC(O2)=0$: the COR_N fragment is removed from the simulation box leaving only the O1 atom bridging the Fe atoms (Fe distances, not shown, are 2.00 and 2.04 Angstrom); (3-3) residue in which $IC(O1)=1$ and $IC(O2)=0$. Iron, oxygen, carbon, and hydrogen atoms are represented by green, red, yellow, and cyan balls, respectively.