Electronic Supplementary Material

Chemical reactions of oily sludge catalyzed by iron oxide under supercritical water gasification condition

Houjun Zhang[1], Fang Chen[1], Jipeng Xu[1], Jinli Zhang[1], You Han (✉)[1,2]

1 School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

2 Tianjin Key Laboratory of Membrane Science and Desalination Technology, Tianjin University, Tianjin 300072, China

E-mail: yhan@tju.edu.cnSimulation temperature

Voter et al.[1] had presented a method that raising the temperature could accelerate the reaction process with extending the time scale by orders of magnitude, which has become a common simulation strategy for ReaxFF MD in a limited time scale. Likewise, according to Arrhenius equation ($k=Ae^{-E_a/(k_BT)}$), raising temperature could accelerate the reaction rate without changing the activation energy barrier, which means the higher the temperature, the faster the reaction happens, and the shorter the time it takes to reach chemical equilibrium. Thus, the chemical reaction could reach equilibrium in a limited time scale compared with the reaction time at normal reaction temperature. For example, Xia et al.[2] investigated the depolymerization process and reaction pathways of scrap tires in SCW condition via ReaxFF MD, and the weight percentages of solid residues combined experiments and

simulations at different temperature (473.15 – 703.15 K vs 1400 – 2600 K) and reaction times (min vs ps) summarizing in the equation:

$$Tr = \frac{Ts + 3087.41}{7.94}$$

so the phenomenon in the smaller time scale and higher temperature simulations can match the phenomenon in the experiments with larger time scale and lower temperature. Wang et al.[3] investigated the carbonization of C_2H_4 on iron nanoparticles at 2500 K and ns scale using ReaxFF MD. Jin et al.[4] adopted a temperature of over 3500 K to figure out the coal gasification process with ns scale in SCW by ReaxFF MD. Zhang et al.[5] applied 3000 K and 800 ps for studying the mechanism of naphthalene degradation on iron oxide in SCWG process. Herein, the simulation always adopts higher temperature in limited time scale. Furthermore, the addition of catalyst could moderate the extreme operation conditions. Therefore, the temperature selected in this study was 2300 K, which is lower compare to the above works.

Descriptions for Figure 10(a) and 10(d)

With the addition of Fe clusters into the system, Fe clusters would be adsorbed on the surface of Fe_2O_3 catalyst providing more active sites, it can adsorb not only reactants, but also more H_2O molecules to generate more ·H and ·OH radicals, the intuitive phenomena are that the amounts of H_2O molecules are decreased and the output of H_2 molecules is risen. And the generation of CO_2 is reliable on sufficient lattice oxygen, and the exposed lattice oxygen is decreased when Fe clusters are

adsorbed on Fe_2O_3, then, large amounts of ·H radicals are generated due to more Fe active sites exposed, which reduces the probability of CO being oxidized to form CO_2. Herein, Figure 10(a) and 10 (d) could exhibit the synergistic effect.

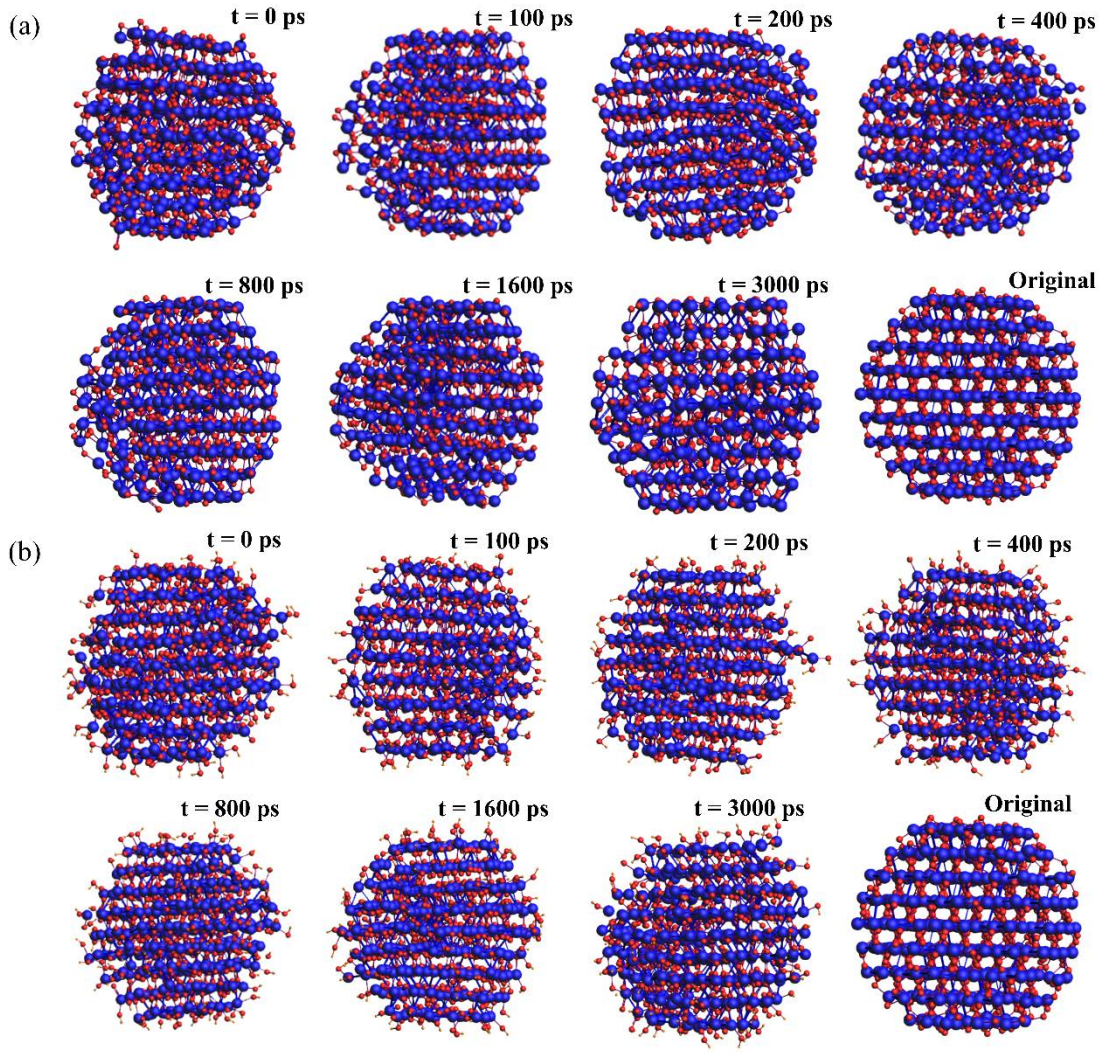

Figure S1**.** Change of crystal morphology of Fe_2O_3 during (a) pyrolysis; (b) SCW conditions

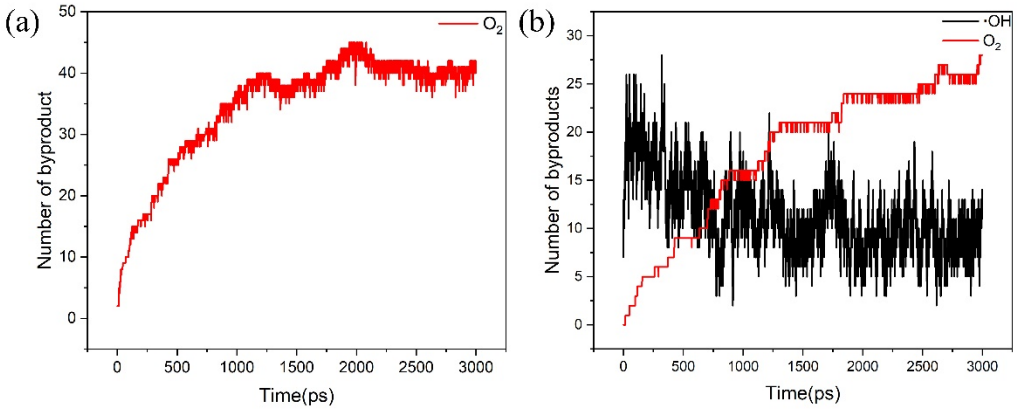

Figure S2. Byproducts produced by (a) pyrolysis; (b) SCW conditions of Fe_2O_3 crystal

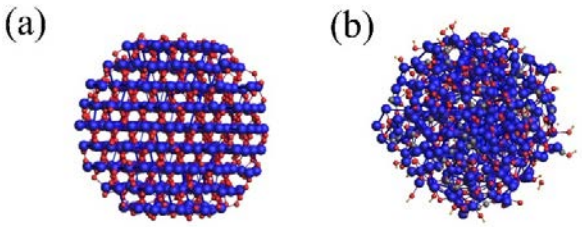

Figure S3. Morphology of (a) fresh; (b) used catalyst;

Reference:

1. Sørensen MR, Voter AF. Temperature-accelerated dynamics for simulation of infrequent events. The Journal of Chemical Physics, 2000, 112: 9599-9606

2. Yan S, Xia D, Zhang X, Jiang B. A complete depolymerization of scrap tire with supercritical water participation: a molecular dynamic simulation study. Waste Management, 2019, 93: 83-90

3. Wang X, Xue X, Zhang C. Early events of the carburization of Fe nanoparticles in ethylene pyrolysis: reactive force field molecular dynamics simulations. Journal of Physical Chemistry C, 2018, 122: 10835-10845

4. Jin H, Xu B, Li H, Ku X, Fan J. Numerical investigation of coal gasification in supercritical water with the ReaxFF molecular dynamics method. International Journal of Hydrogen Energy, 2018, 43: 20513-20524

5. Han Y, Ma T, Chen F, Li W, Zhang J. Supercritical water gasification of naphthalene over iron oxide catalyst: a ReaxFF molecular dynamics study. International Journal of Hydrogen Energy, 2019, 44: 30486-30498