

A ReaxFF Study for Hacac Interaction on Al₂O₃ Surface in Area-Selective ALD

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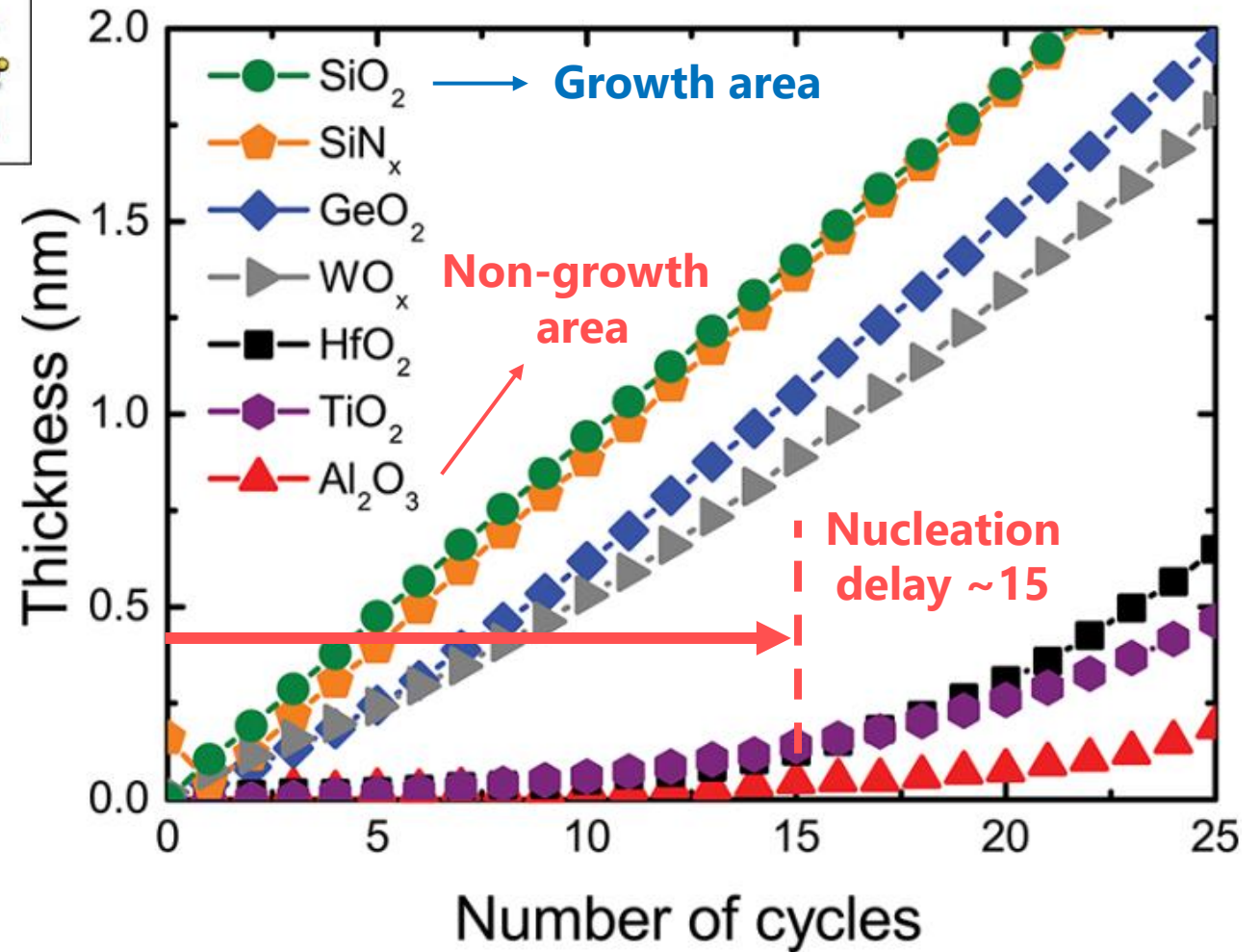
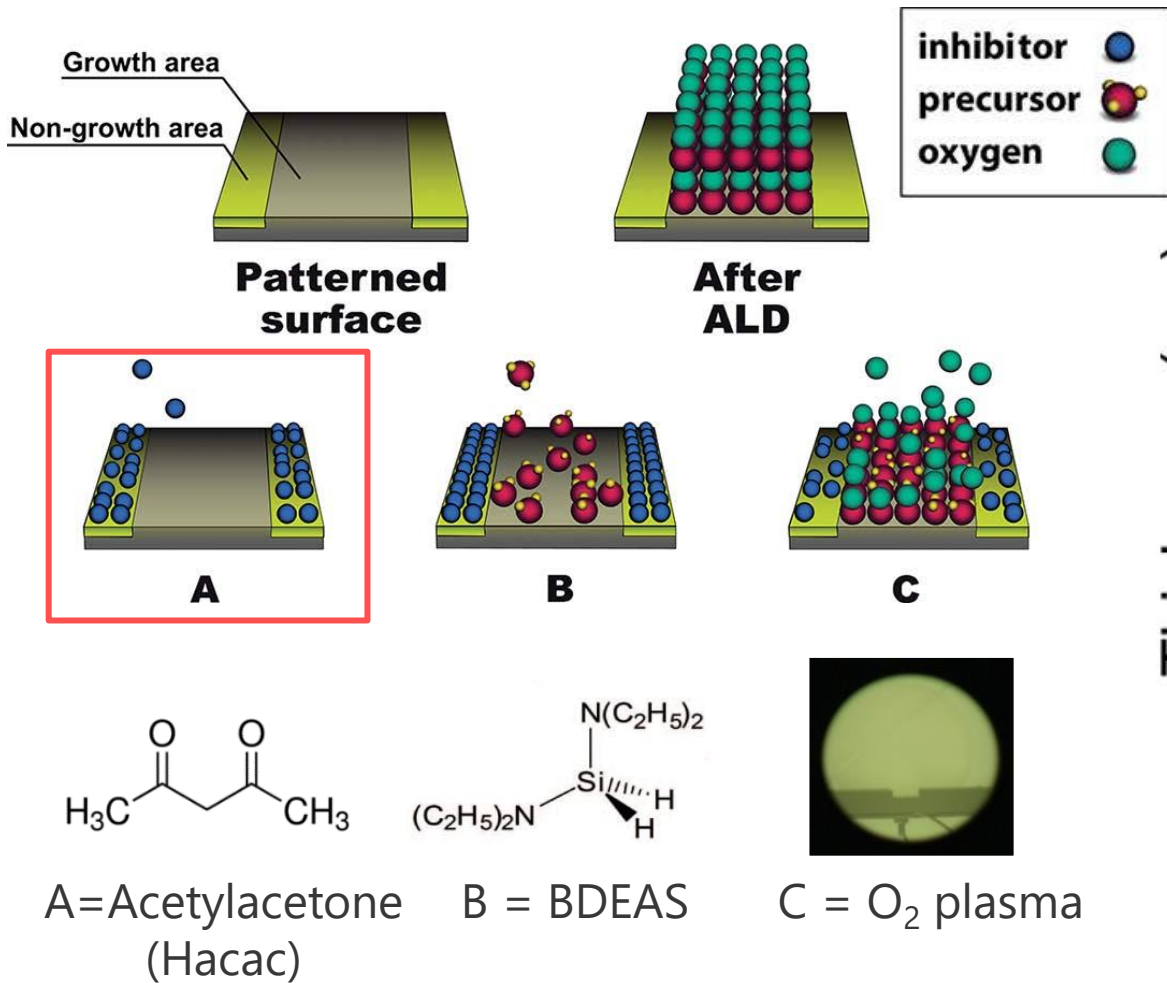
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Atomic Scale Processing (AP)

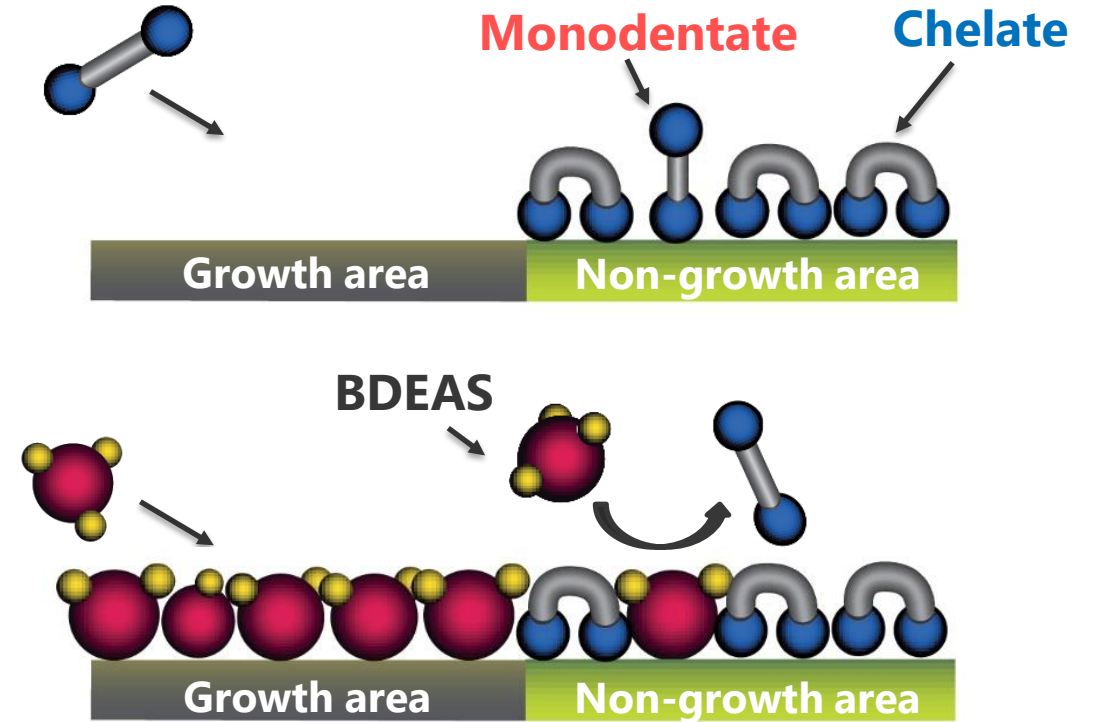
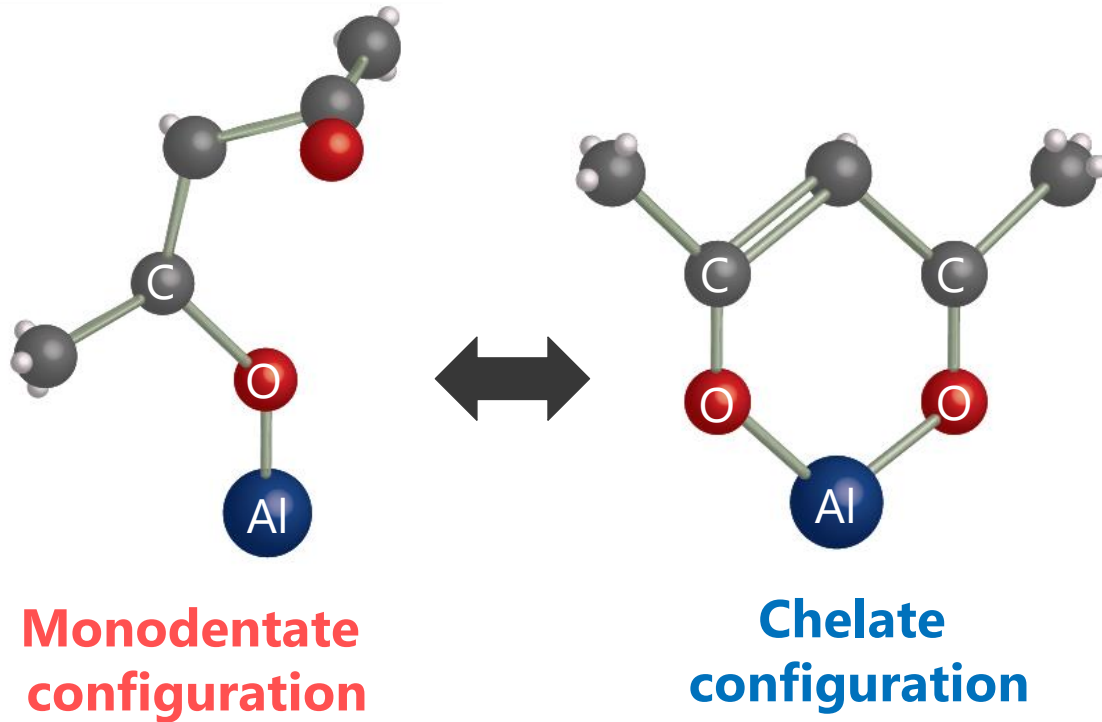
Area Selective Processing and Patterning

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In order to increase the selectivity, the blocking performance by Hacac is critical.

[1] ACS Nano 2017, 11, 9303–9311



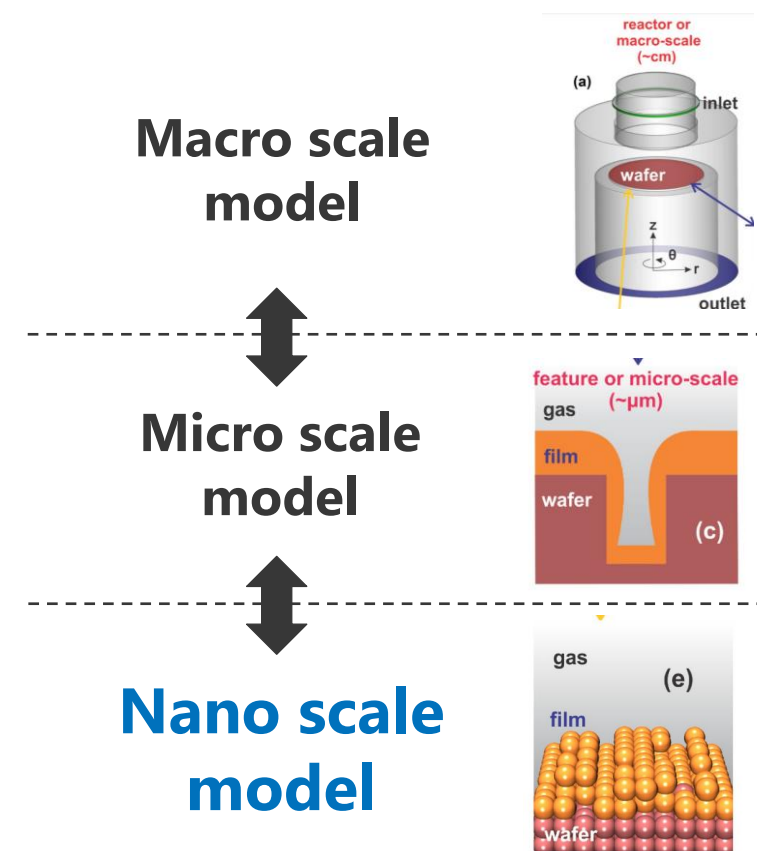
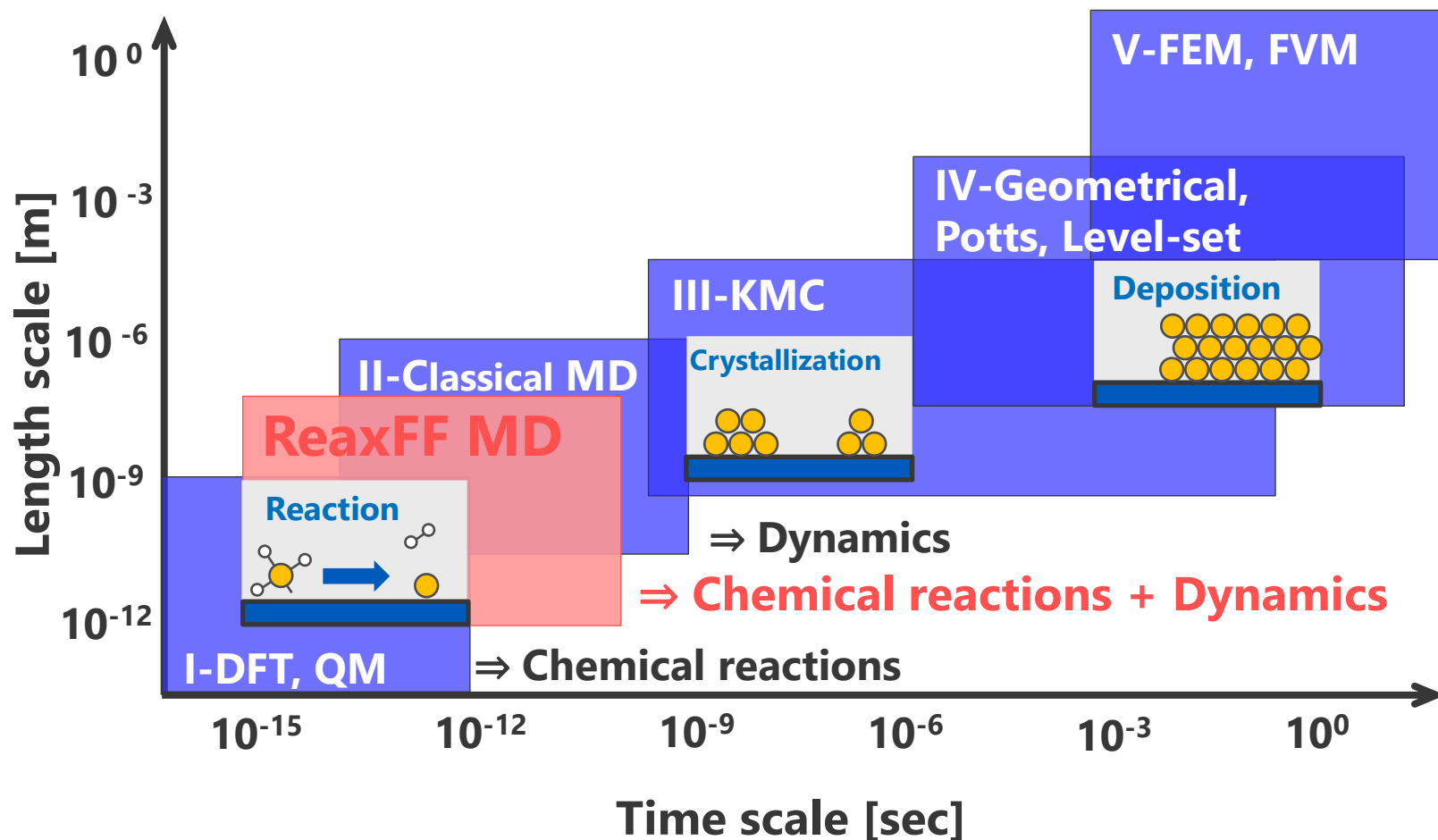
- A mixture of chemisorption in monodentate and chelate configuration has been observed.
- The monodentate configuration is relatively reactive with BDEAS, causing the loss of selectivity.

We aim to understand the dynamics of Hacac chemisorption on the $\text{OH-Al}_2\text{O}_3$ surface with relative densities of the chelate or monodentate configurations.

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ReaxFF MD is able to simulate dynamics and chemical reactions in atomic scale.

[3] J. Phys. Chem. A 2001, 105 (41), 9396–9409

Newton's equations of motion

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i = -\nabla \sum_{j=1, i \neq j}^N E_{ij} \rightarrow E_{system}$$

$$E_{system} = \underbrace{E_{bond} + E_{angle} + E_{tors} + E_{conj} + E_{over} + E_{under}}_{\text{Bond order dependent}} + \underbrace{E_{coa} + E_{pen} + E_{lp} + E_{C2} + E_{triple} + E_{H-bond} + E_{vdWaals} + E_{Coulomb}}_{\text{Bond order independent}}$$

What is Bond order (BO)?

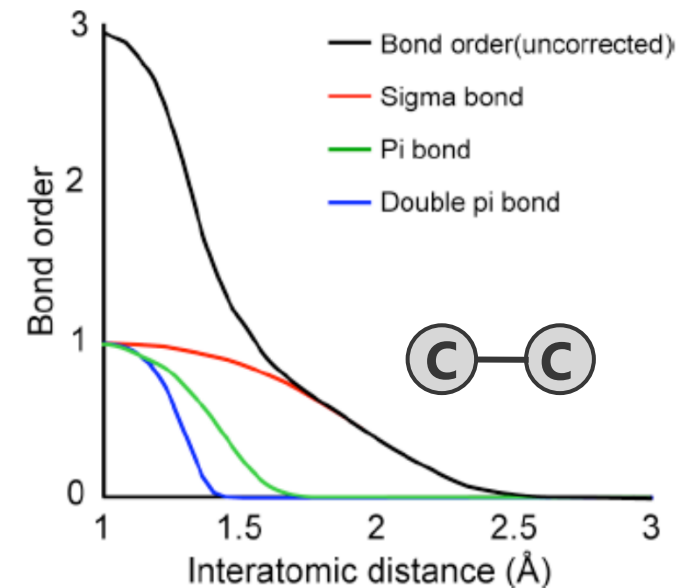
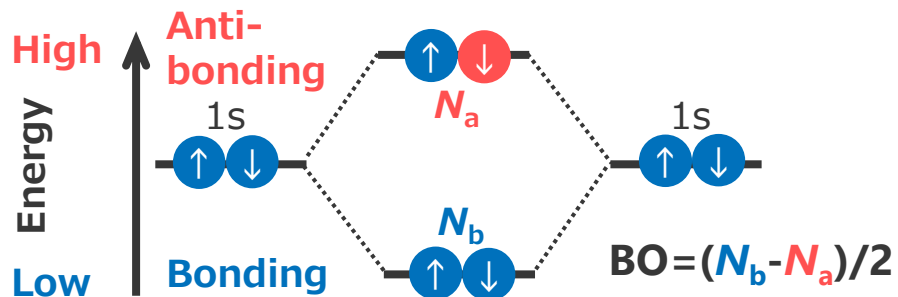
- Difference in the number of electrons in the bonding/anti-bonding orbitals
- A BO value that quantitatively expresses the strength of a chemical bond
- **BO is sum of the partial σ , π , and $\pi\pi$ bonds contributions**

$$BO'_{ij} = BO'_{ij}{}^{\sigma} + BO'_{ij}{}^{\pi} + BO'_{ij}{}^{\pi\pi}$$

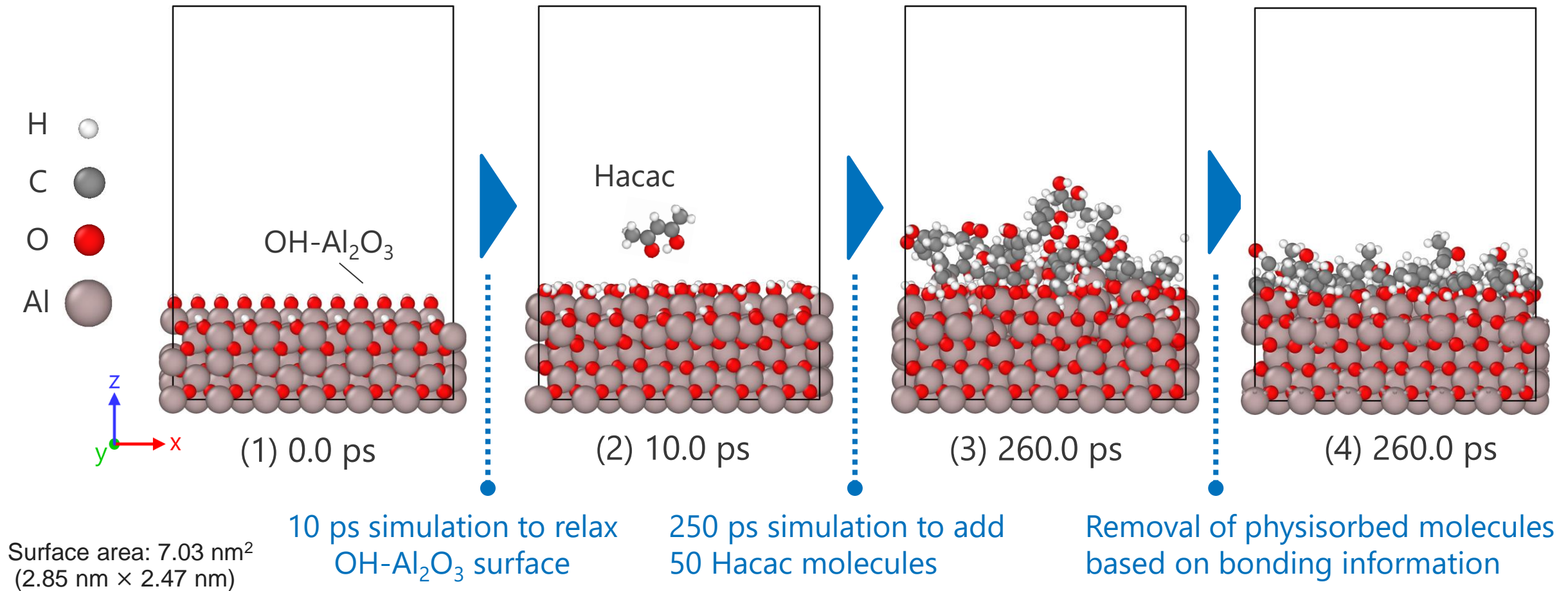
$$= \exp \left[p_{bo1} \cdot \left(\frac{r_{ij}}{r_o^{\sigma}} \right)^{p_{bo2}} \right] \sigma \text{ bond}$$

$$+ \exp \left[p_{bo3} \cdot \left(\frac{r_{ij}}{r_o^{\pi}} \right)^{p_{bo4}} \right] \pi \text{ bond}$$

$$+ \exp \left[p_{bo5} \cdot \left(\frac{r_{ij}}{r_o^{\pi\pi}} \right)^{p_{bo6}} \right] \pi\pi \text{ bond}$$



We developed the new ReaxFF to describe Hacac interaction on OH-Al₂O₃ surfaces.



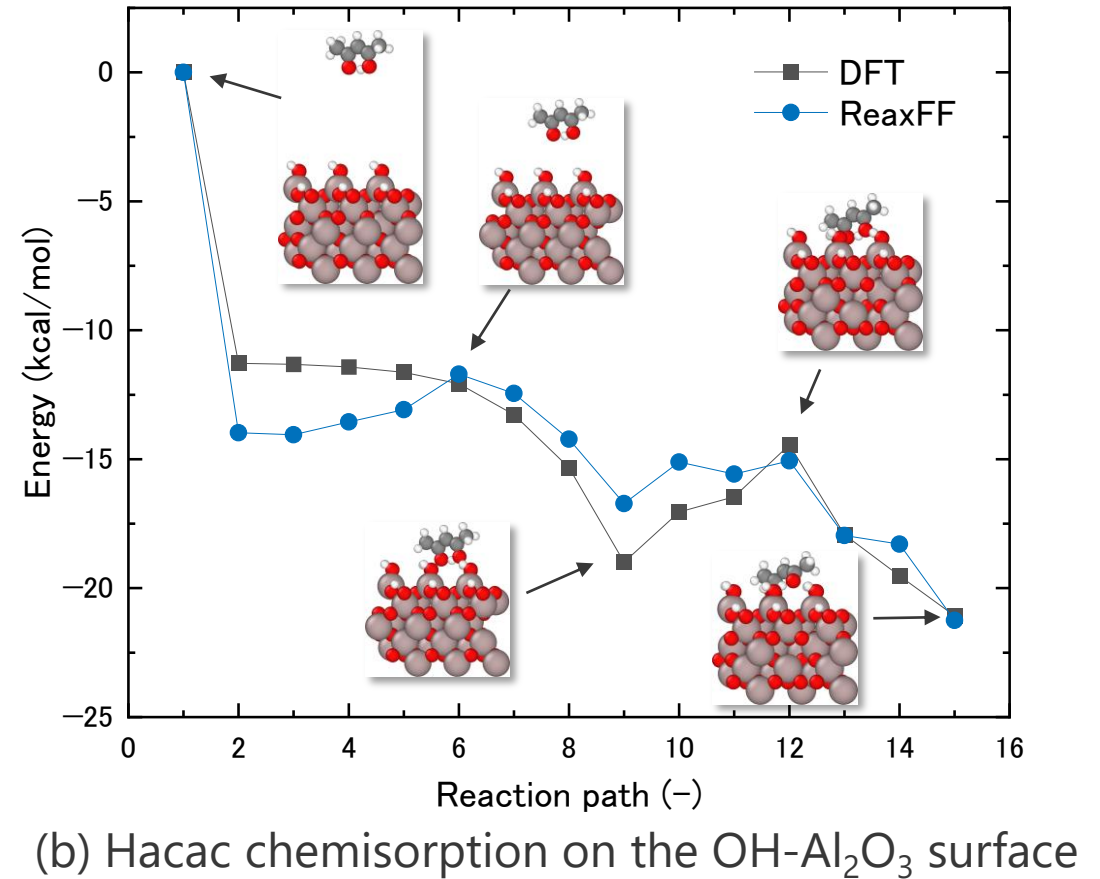
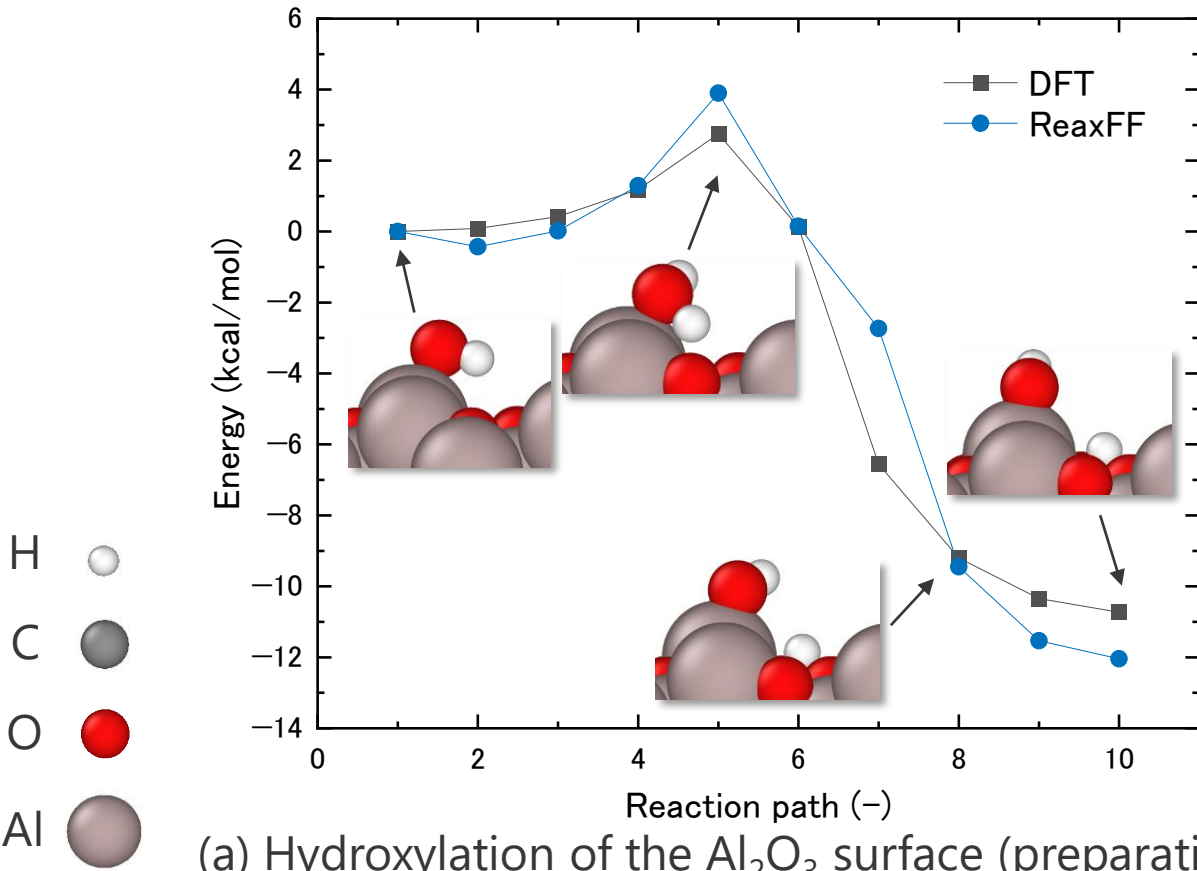
ASD simulation for Hacac on OH-Al₂O₃ surface was performed with ReaxFF MD.

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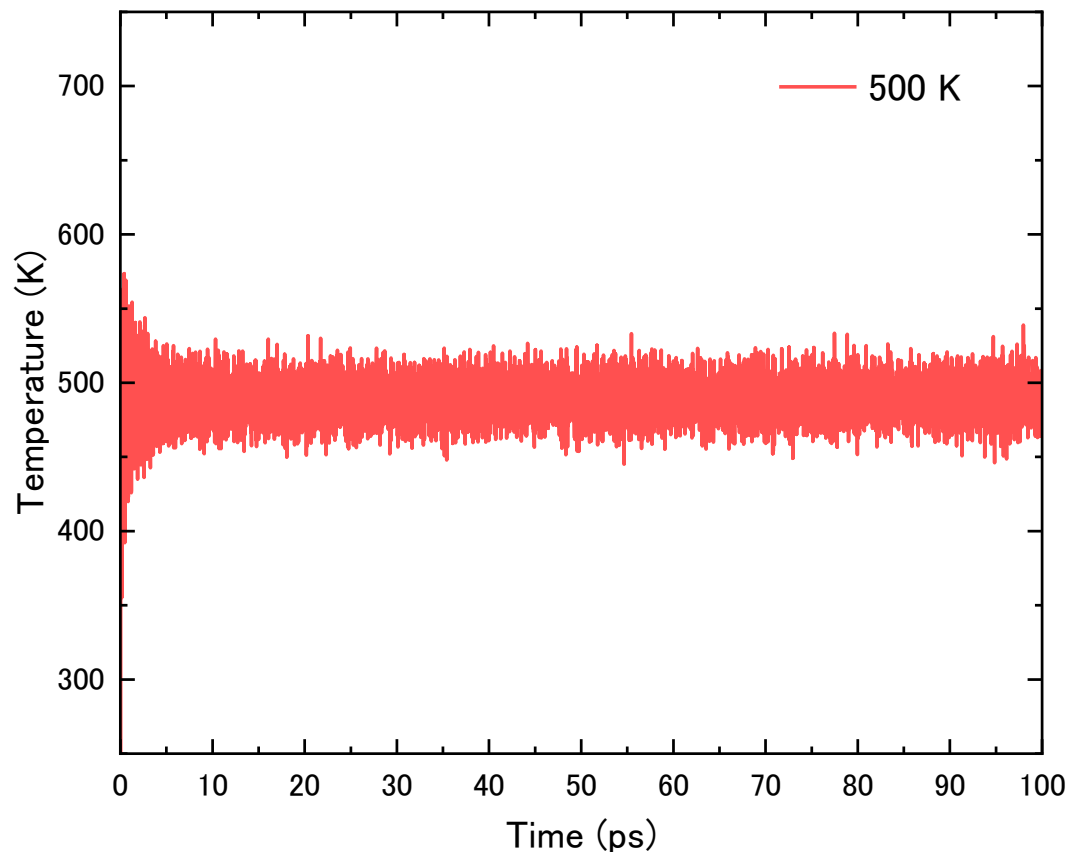
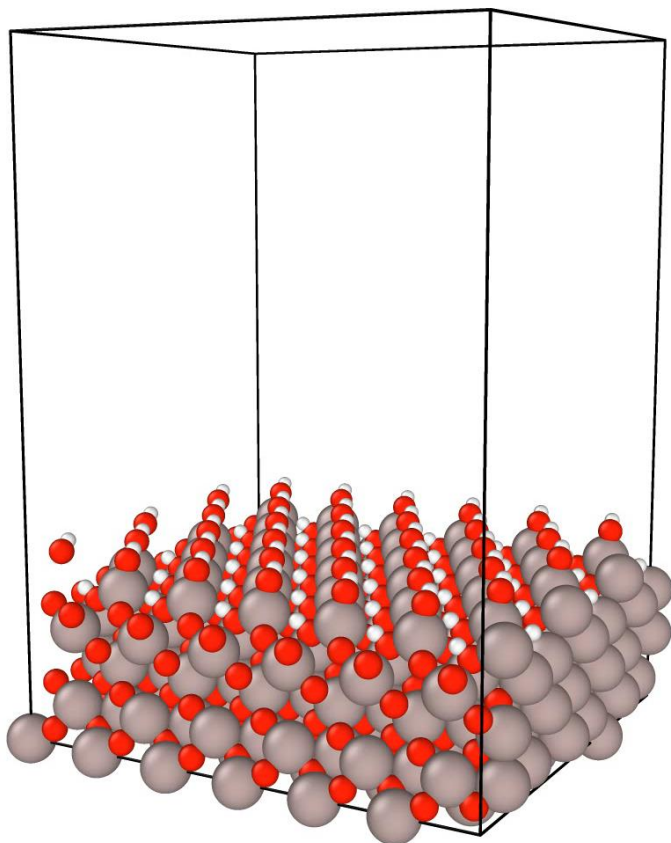
The existing C/H/Al/O force field^[4] was trained to describe Hacac chemisorption on OH-Al₂O₃ surface.



A new ReaxFF shows a good agreement with the energy profile by DFT methods.

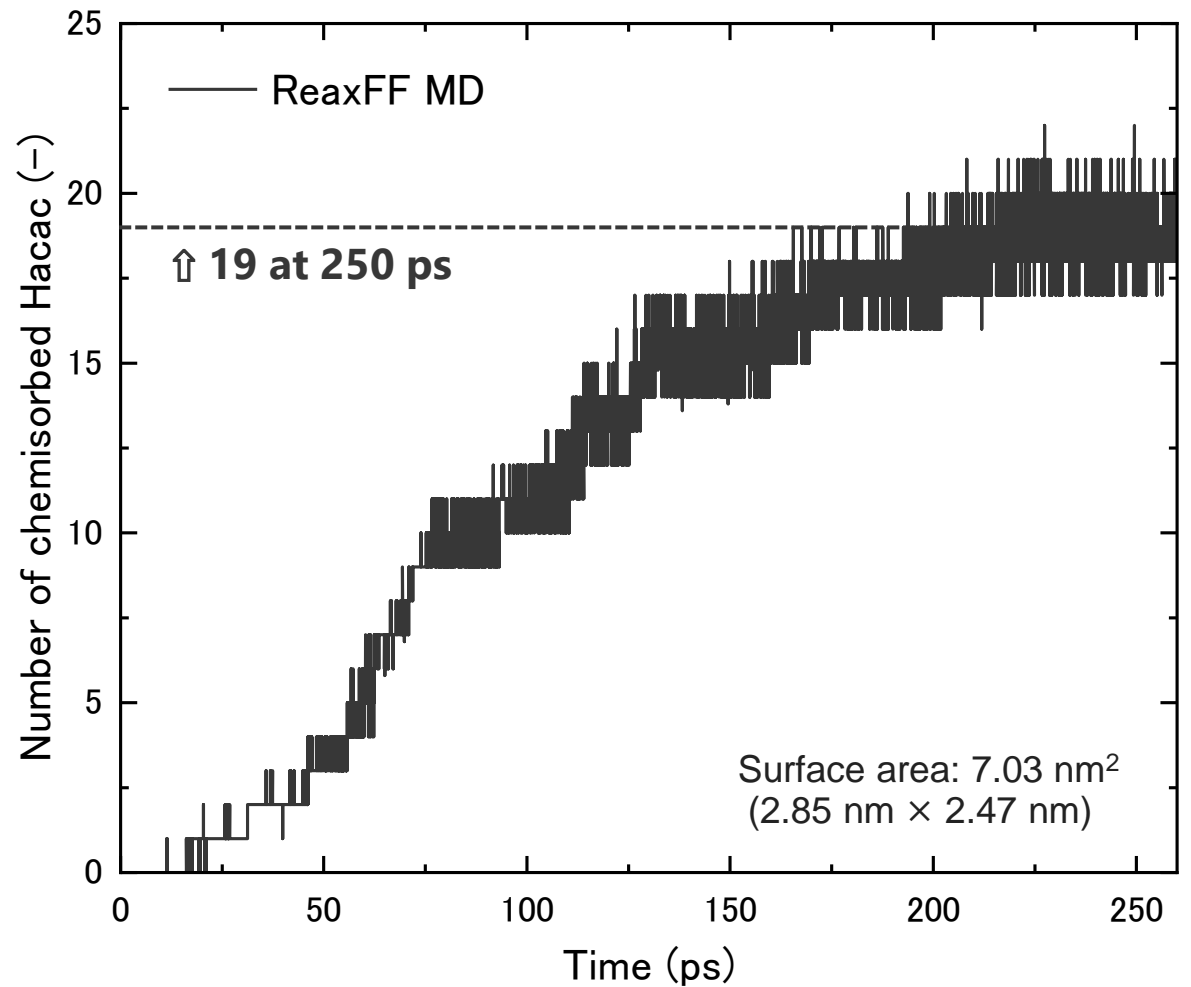
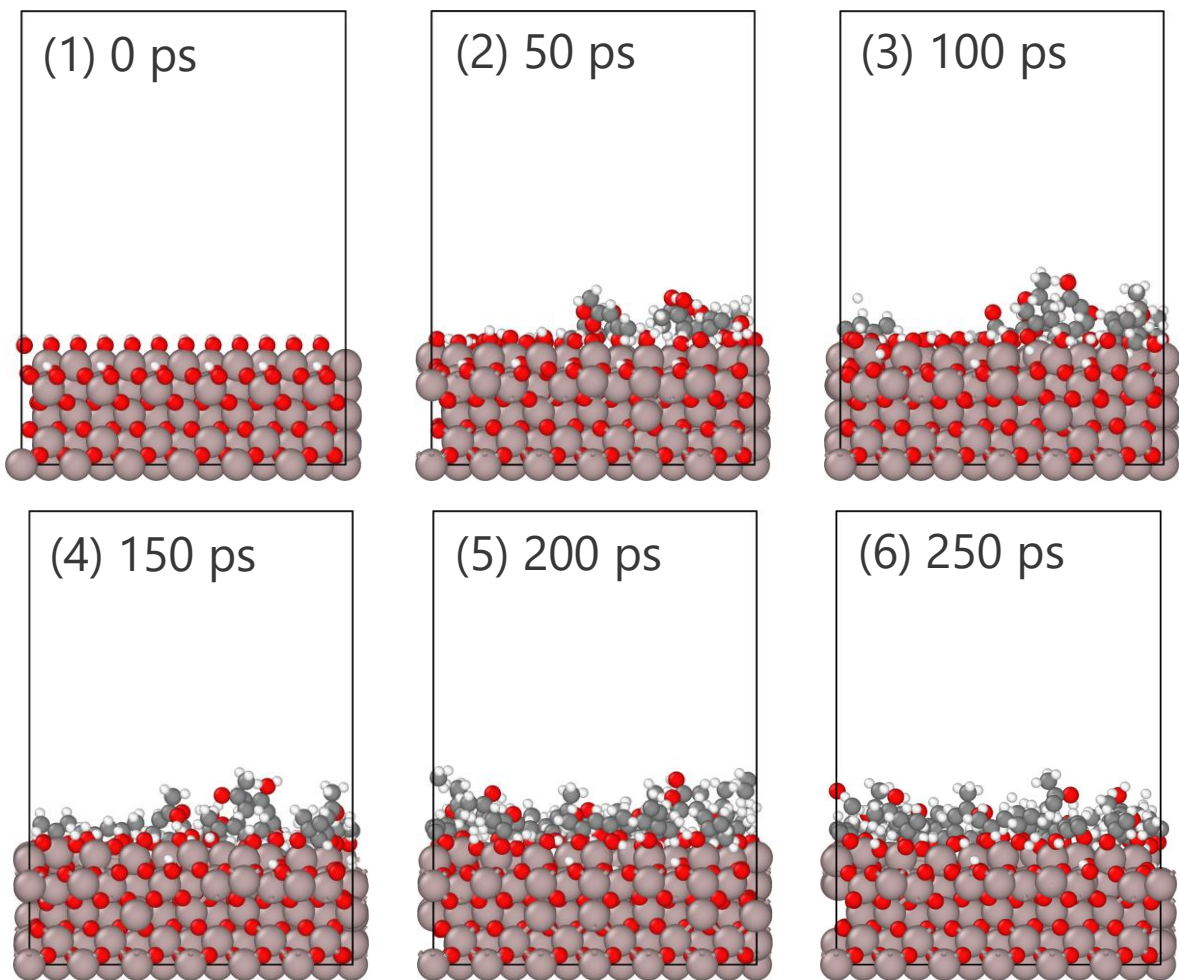
[4] J. Phys. Chem. C 2016, 120, 17, 9464–9474

Before simulating the Hacac interaction, we check the thermal stability of the OH- Al_2O_3 surface.

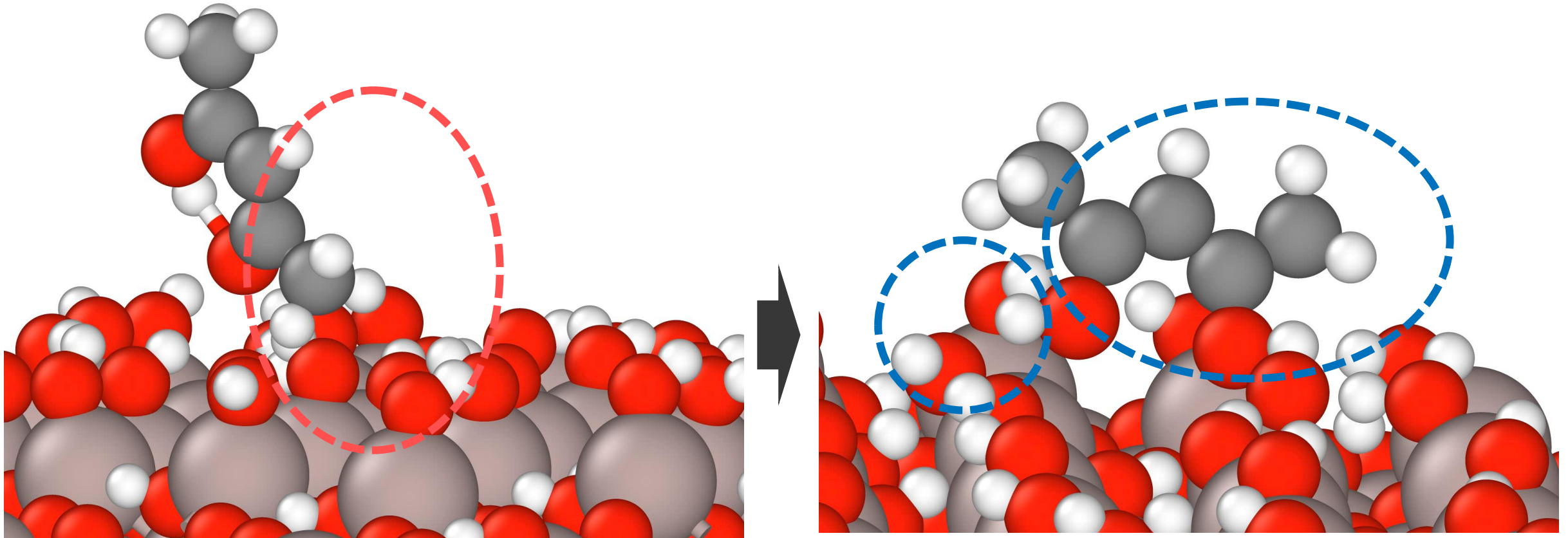


- 500 K is slightly higher than the experimental temperature at 150°C to accelerate the surface events^[1].
- The temperature of the surface is well controlled within ± 50 K over time.

The developed ReaxFF is able to simulate the stable OH- Al_2O_3 surface at 500 K.



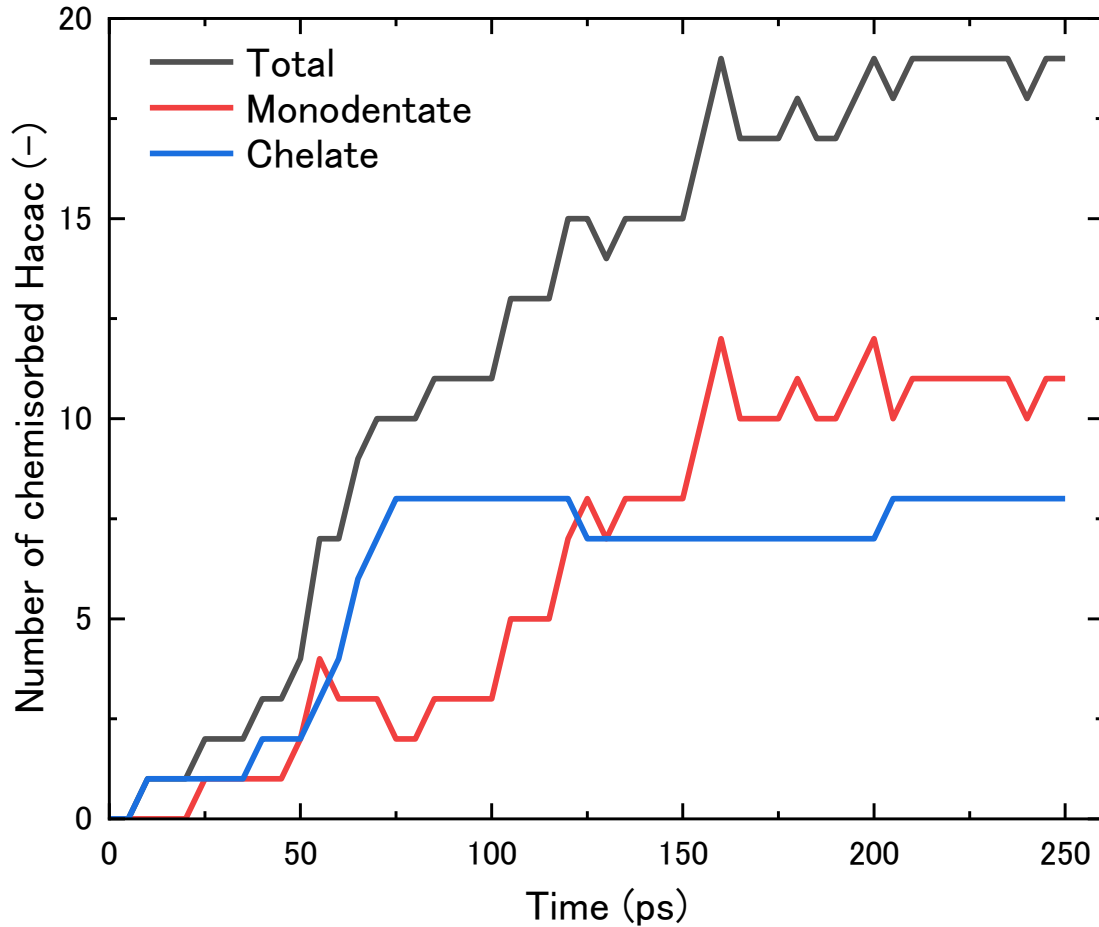
Hacac is sequentially chemisorbed, and surface is saturated with 19 Hacac molecules.



(a) Chemisorption in monodentate configuration by creating a new Al-O bond

(b) Chemisorption in chelate configuration by transferring Hydrogen to the next site

Hacac chemisorbed in Monodentate changes to Chelate by transferring an H atom.



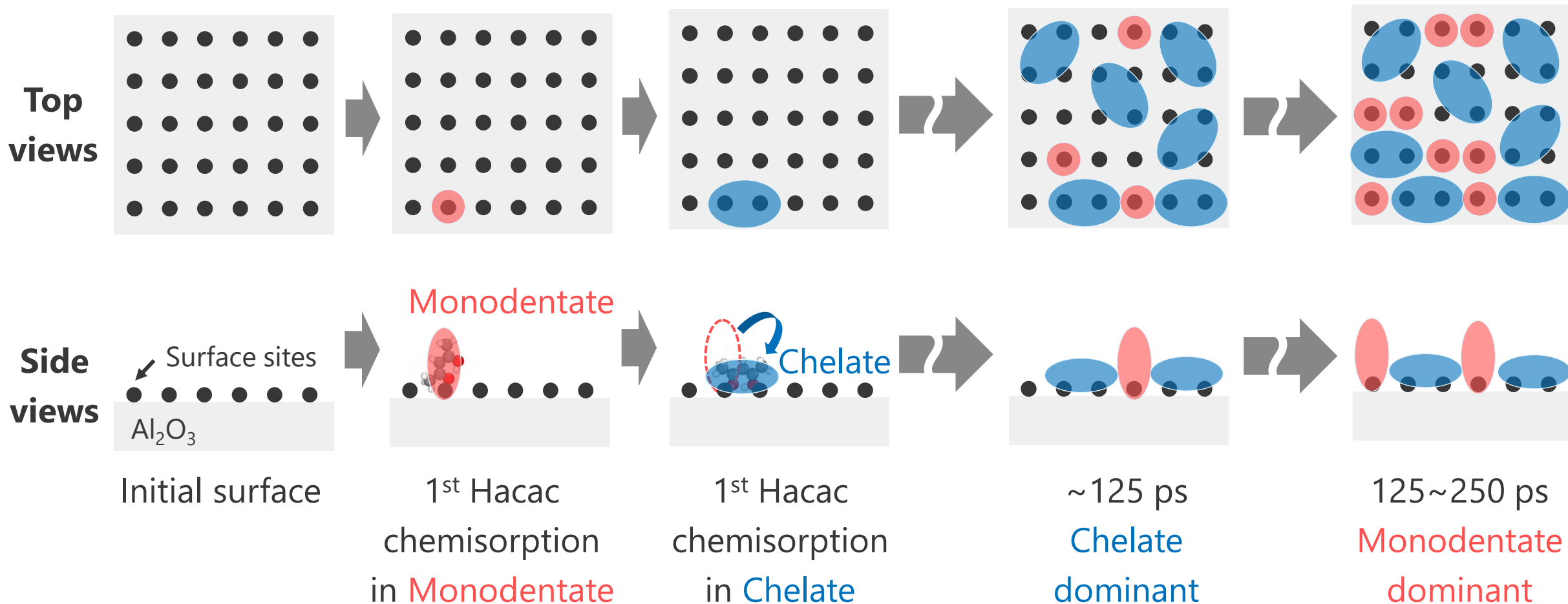
The number of chemisorbed Hacac with the time

- The surface is saturated with chelate after 75 ps, then the new Hacac can only chemisorb in monodentate.
- In the first 125 ps, the chelate configuration is dominant.

The occupation mechanisms

- The chelate preferentially occupies surface sites, but because of the large footprint, unoccupied sites remain.
- The remaining sites are gradually occupied with the monodentate configurations, saturating the surface.

The surface is initially dominated by Chelate and then Monodentate.



The dynamics of Hacac chemisorption are clarified by ReaxFF MD simulations.

Conclusions

We performed ReaxFF MD simulations to understand the dynamics of Hacac chemisorption on the OH-Al₂O₃ surface with relative densities of the chelate or monodentate configurations.

- **Confirmed by ReaxFF simulations**

- Hacac adsorbs in a mixture of monodentate and chelate configurations
- Hacac chemisorbed in monodentate configuration changes to chelate by transferring H

- **Insights from ReaxFF MD simulations**

- Initially the surface is dominated by Hacac in chelate configuration
- Hacac adsorbs in monodentate configuration when the surface becomes crowded



Insight into the dynamics of chemisorption will lead to the development of inhibitors with higher blocking performance

Thank you for your kind attention!

- This work was supported by The Murata Science Foundation in Japan.
- Numerical simulations were performed on the Supercomputer system "AFI-NITY" at the Advanced Fluid Information Research Center, Institute of Fluid Science, Tohoku University.



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