EuroCVD22 – BalticALD16

24-28 June 2019

Luxembourg

How spectator adsorbates affect surface reactivity

Simon D. Elliott, Thomas J. Mustard

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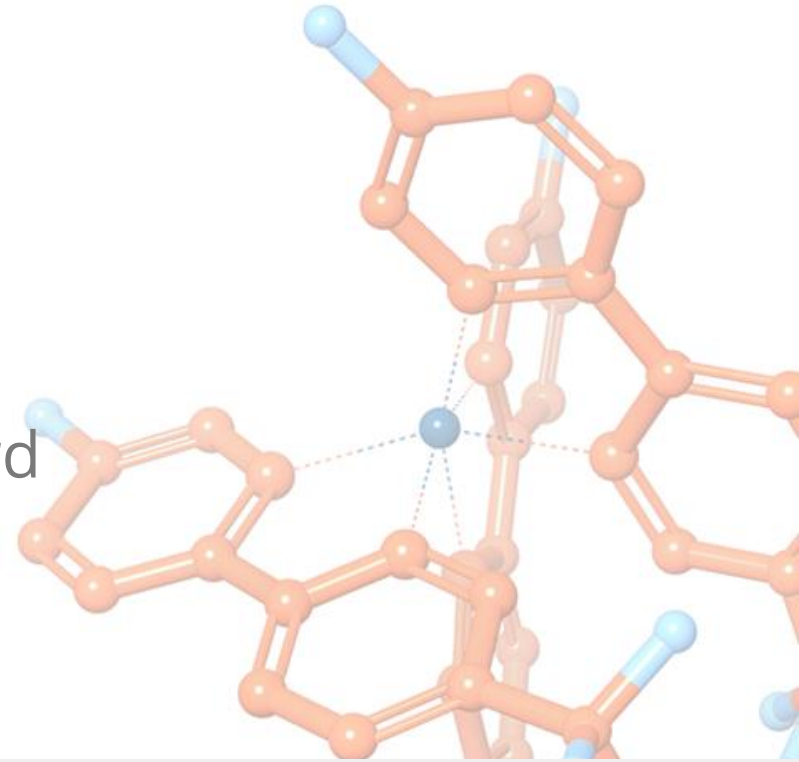


Outline

How spectator adsorbates affect surface reactivity: computing the cooperative effect by automated enumeration of reaction pathways

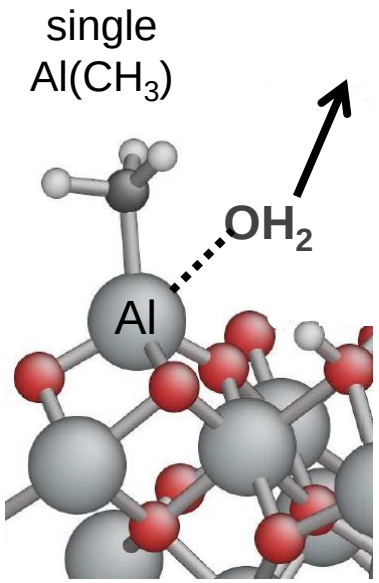
- **What is the cooperative effect?**
- **Cluster model and framework for enumeration**
- **Enumeration of structures for H_2O adsorption**
- **Next step: reactions of adsorbed H_2O**

What is the cooperative effect?

Cooperative effect: neighbouring fragments affect reactivity

DFT calculations of H_2O adsorption to methylated surface during ALD of Al_2O_3

large grey=Al, red=O, white=H, small grey=C



No chemisorption
of single H_2O
to single $Al(CH_3)$

M. Shirazi & S. D. Elliott, Nanoscale, 7, 6311-6318 (2015)

Cooperative effect: neighbouring fragments affect reactivity

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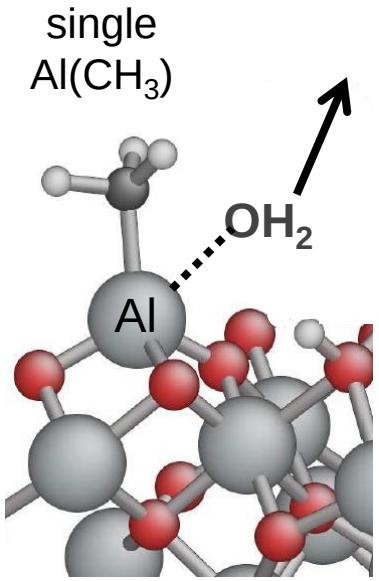

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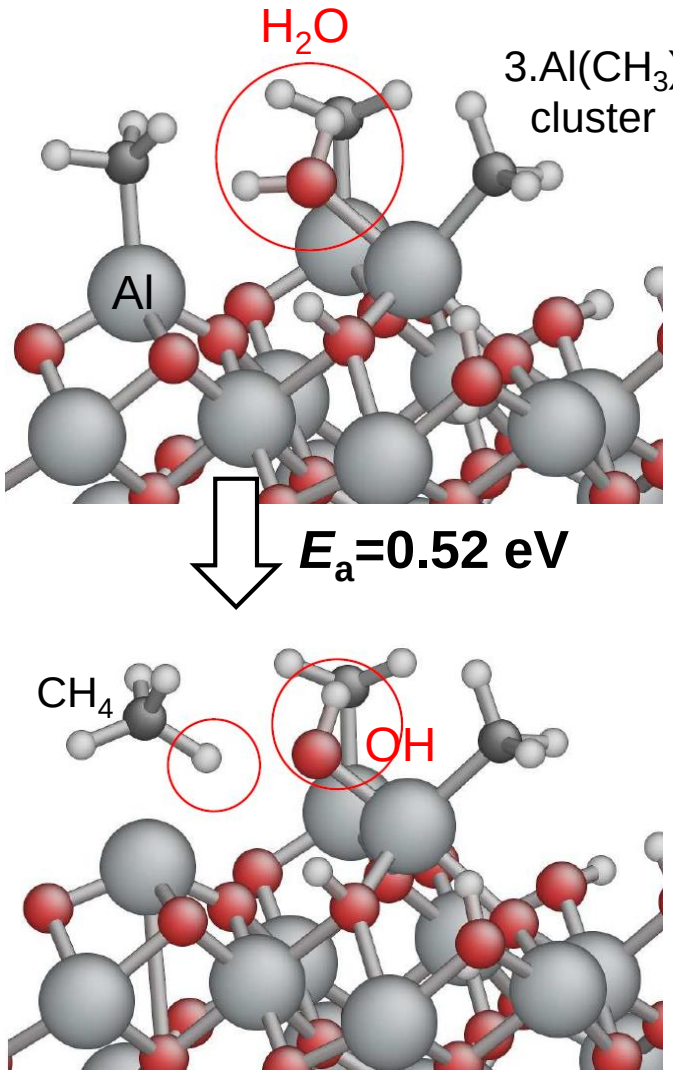

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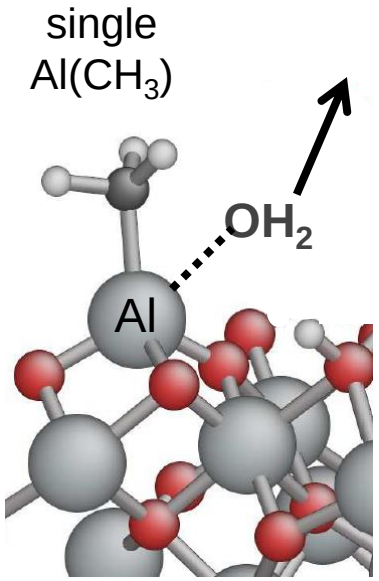

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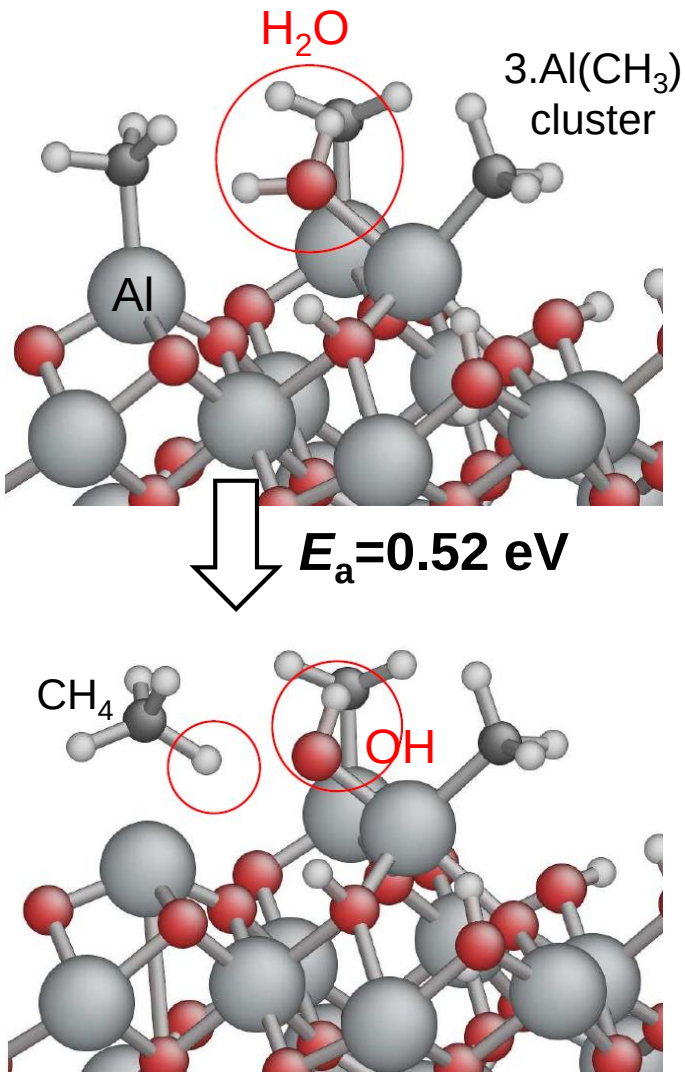

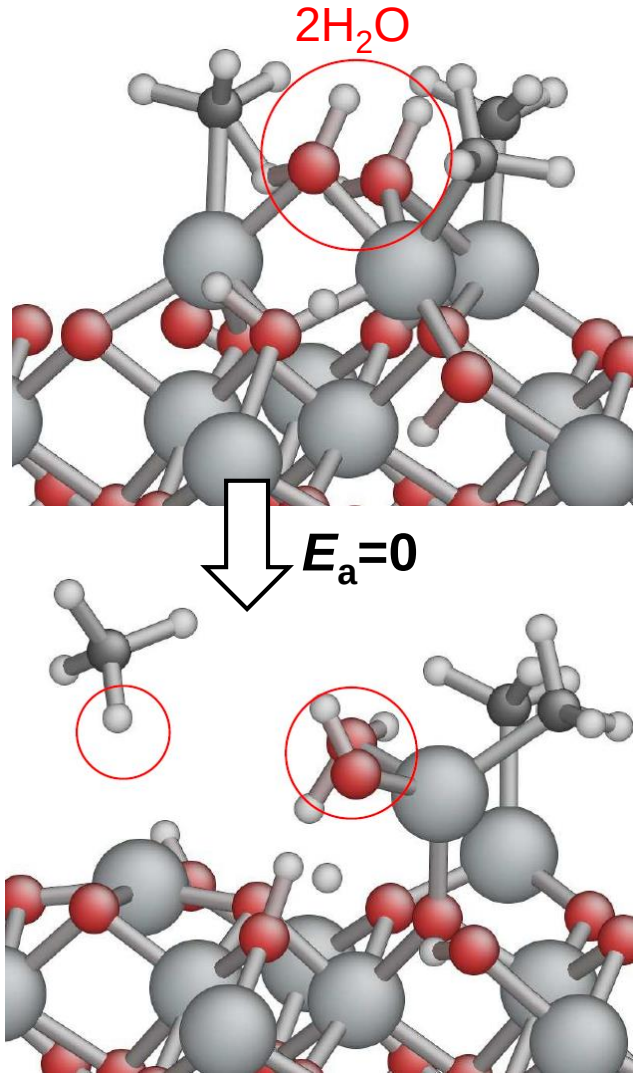

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APPLIED PHYSICS LETTERS 108, 011607 (2016)

What is limiting low-temperature atomic layer deposition of Al_2O_3? A vibrational sum-frequency generation study

V. Vandalon[a)] and W. M. M. Kessels[a)]
Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

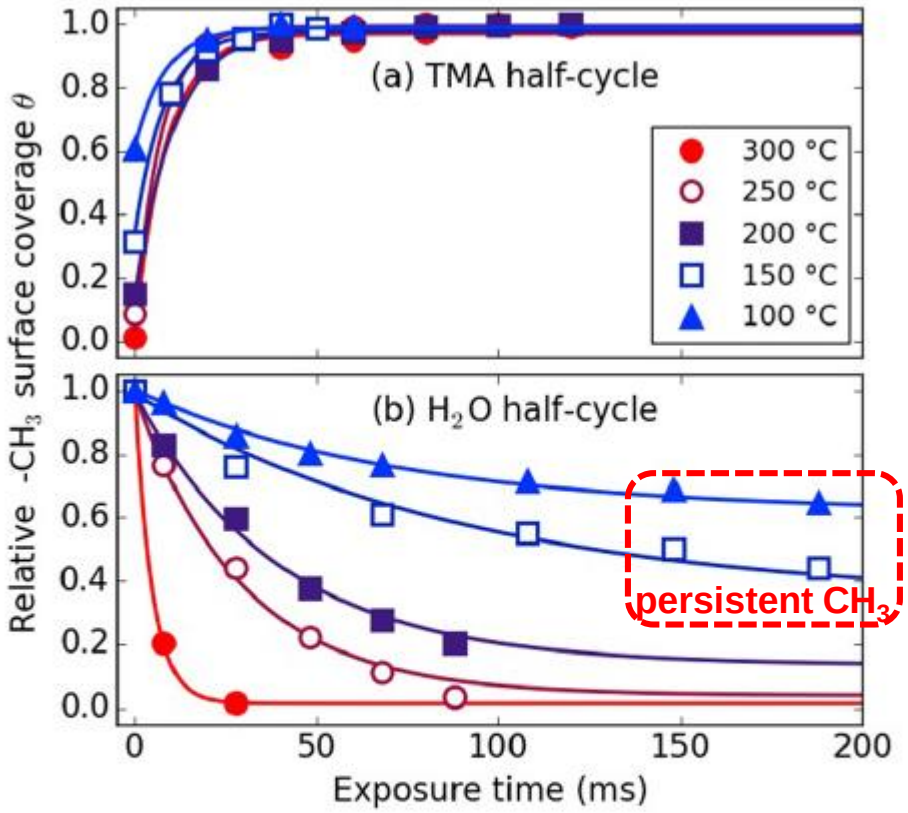


FIG. 3. Relative –CH_3 surface coverage θ, extracted from the BB-SFG spectra as a function of TMA and H_2O exposure for various temperatures. The solid lines represent fits to the data in order to extract information about the reaction kinetics.

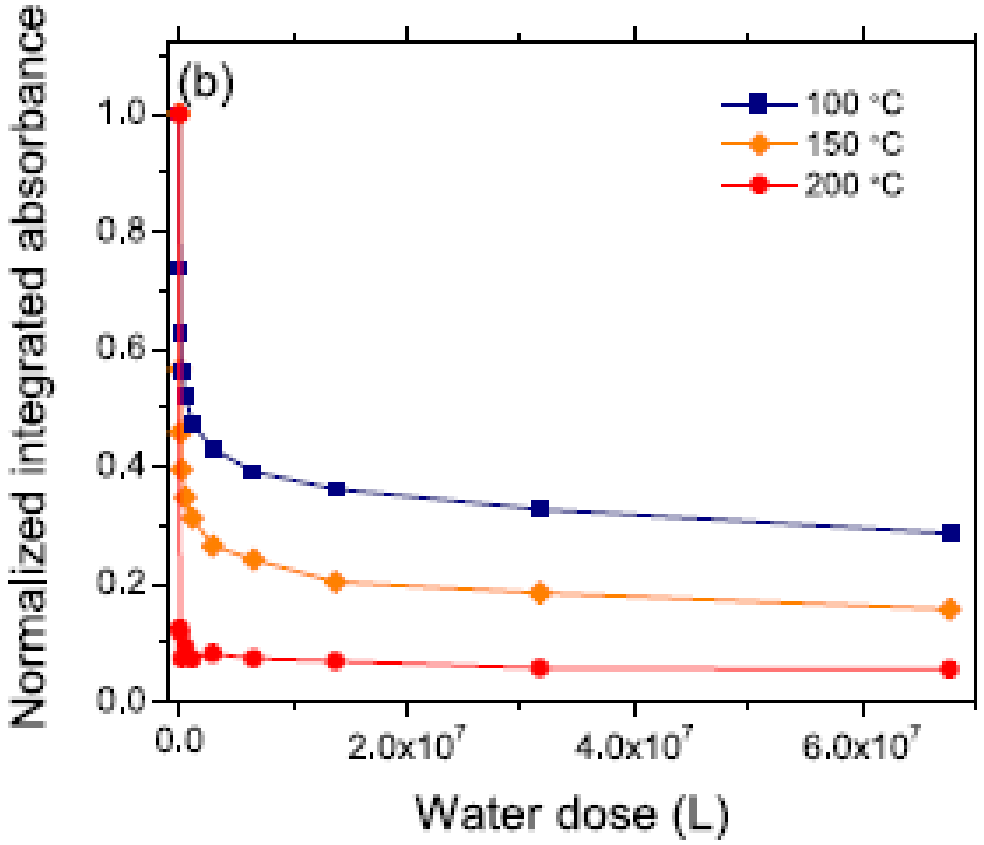
THE JOURNAL OF CHEMICAL PHYSICS 146, 052802 (2017)

Incomplete elimination of precursor ligands during atomic layer deposition of zinc-oxide, tin-oxide, and zinc-tin-oxide

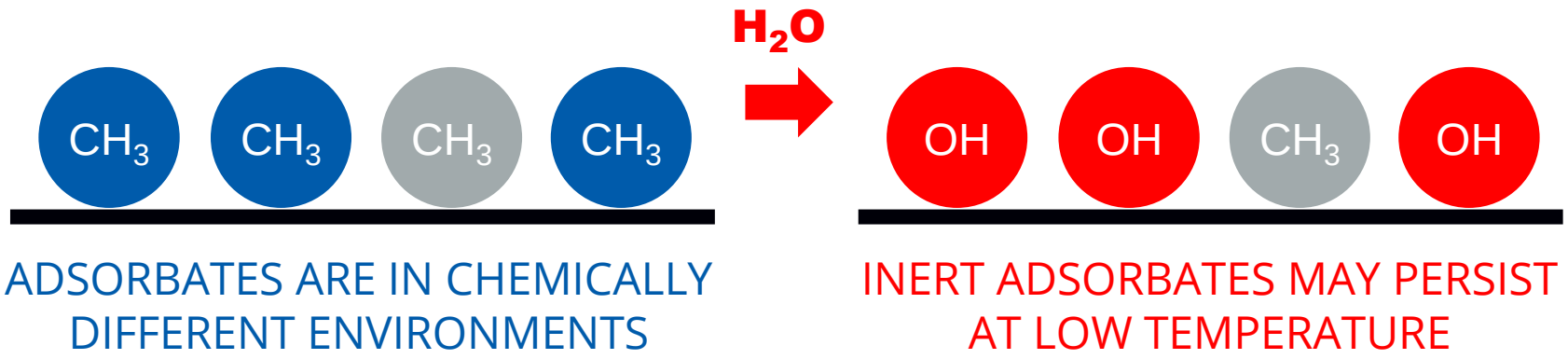
Adriaan J. M. Mackus, Callisto MacIsaac, Woo-Hee Kim, and Stacey F. Bent[a)]
Department of Chemical Engineering, Stanford University, Stanford, California 94305, USA

$Zn(C_2H_5)_2+H_2O \rightarrow ZnO$

Ligand CH detected by FTIR at end of H_2O pulse relative to end of Zn pulse:



Cooperative effect: neighbouring fragments affect reactivity



Open questions:

- Is the effect specific to 4-coordinate Al, or does it occur in other Al coordination environments as well?
- Are neighbouring adsorbates exerting a steric effect, or also electronic?
- Kinetics only, or also thermodynamics?

Challenges for simulation

Rather than modelling…	We must now consider…
isolated molecules	many configurations of co-adsorbates
in small simulation cells	in large simulation cells
on flat smooth crystalline surfaces	on more realistic 3D nanostructured surface regions
yielding one mechanism, one reaction pathway, one activation energy.	potentially producing as many activation energies and pathways as surface geometries that can be imagined.

Automatic enumeration of surface geometries gives a route towards systematically investigating such complex systems, exploiting the power of computational chemistry.

Cluster model and framework for enumeration

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Model of Al_2O_3 surface

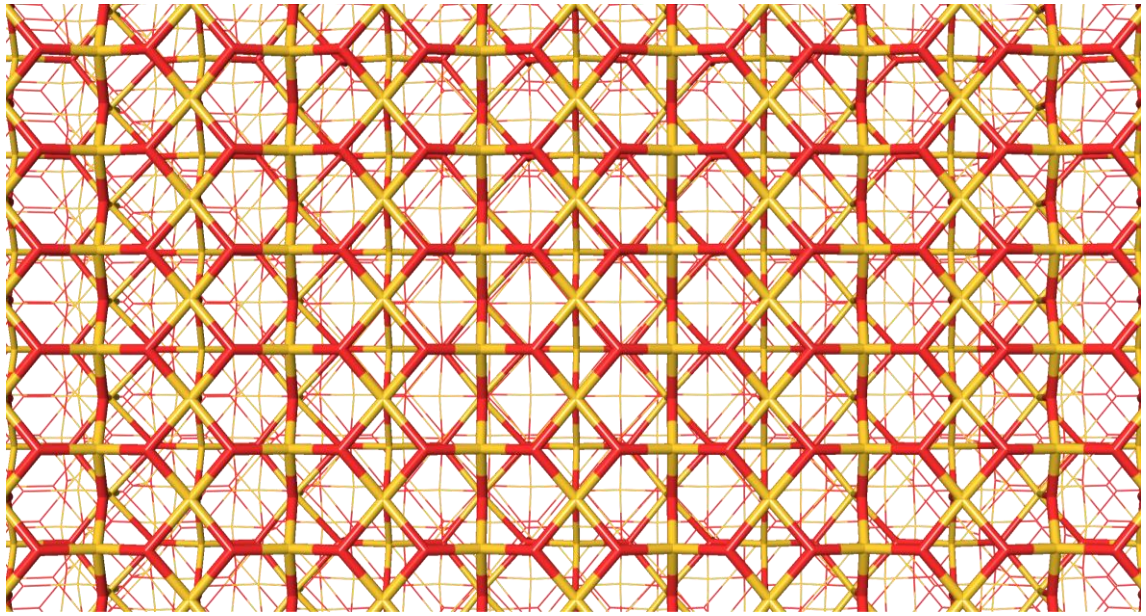
Monoclinic θ-Al_2O_3 C21/m1 (#12) as model of amorphous as-deposited film.

Selected AlO-terminated (1 0 0) surface based on computed surface energies:

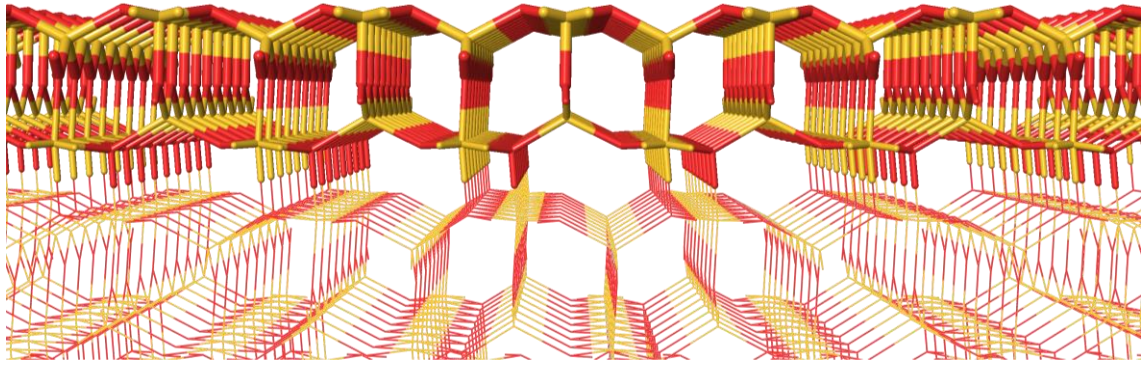
- 0.6 J/m^2 for AlO-terminated (1 0 0)
- 1.1 J/m^2 for O-terminated (1 0 0)
- 1.4 J/m^2 for AlO-terminated (0 0 1)
- 2.3 J/m^2 for O-terminated (0 0 1)

TOP VIEW

Ga=yellow, O=red



SIDE VIEW



Model of Al_2O_3 surface

(1 0 0) surface

- 5-coordinate Al
- 4-coordinate Al

molar volume = 24 Å^3/$AlO_{3/2}$

- Monolayer thickness = (molar volume)$^{1/3}$ = 2.9 Å
- Areal density = (molar volume)$^{-2/3}$ = 6(Al_2O_3)/nm^2

TOP VIEW

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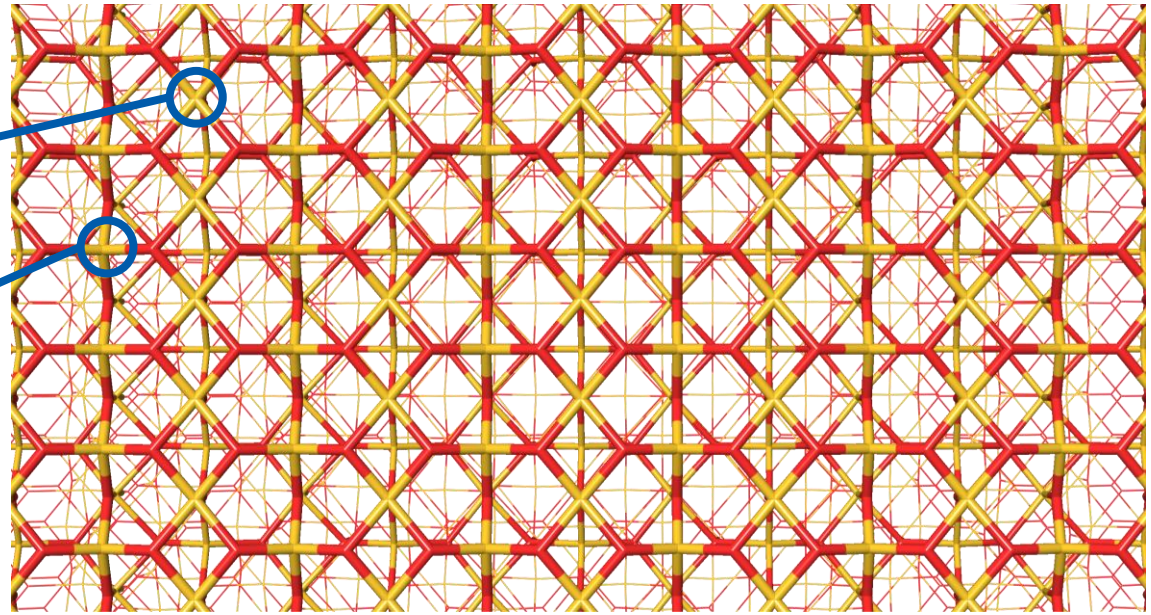

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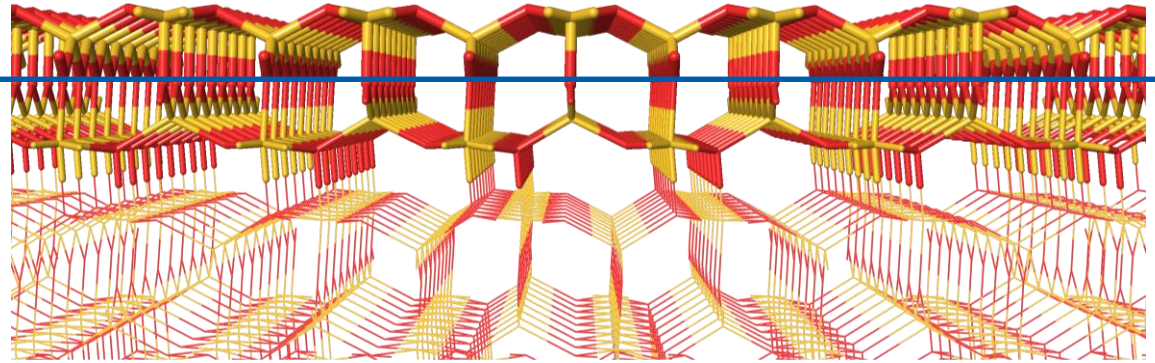

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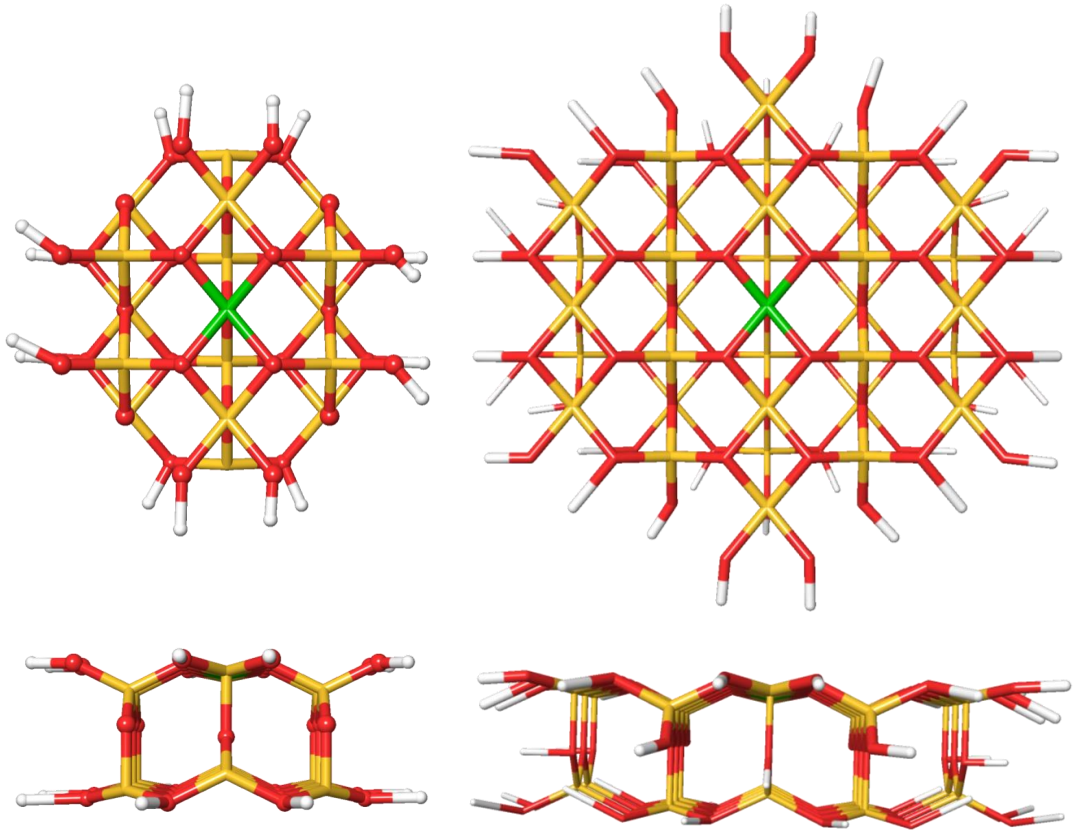
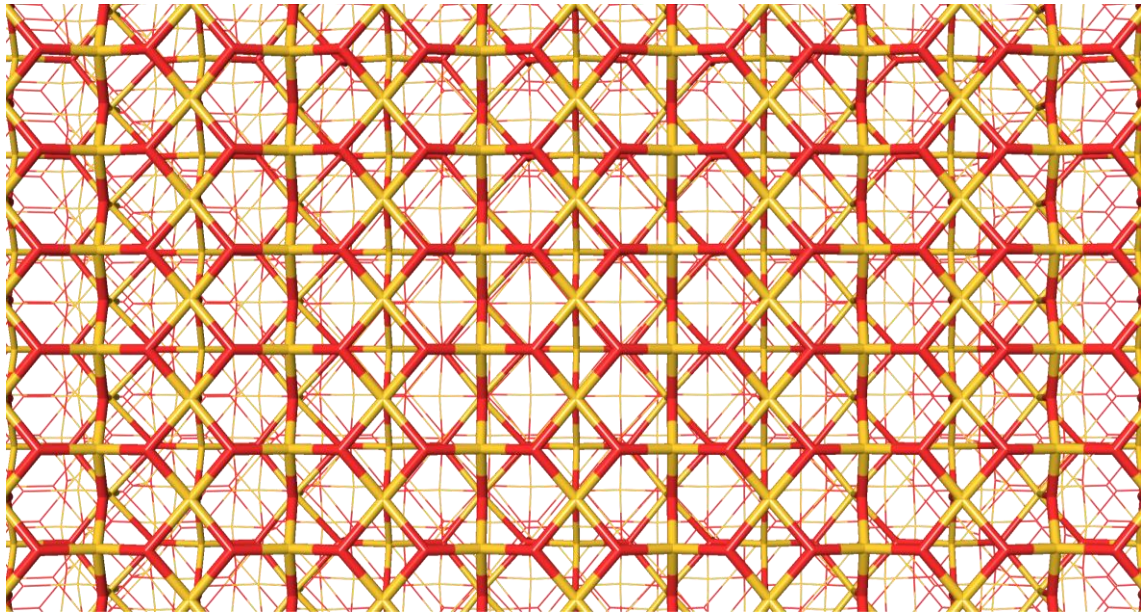


66-atom cluster
area=0.67 nm^2

140-atom cluster
area=1.33 nm^2

TOP VIEW

Ga=yellow, O=red, C=grey, H=white, adsorption site=green



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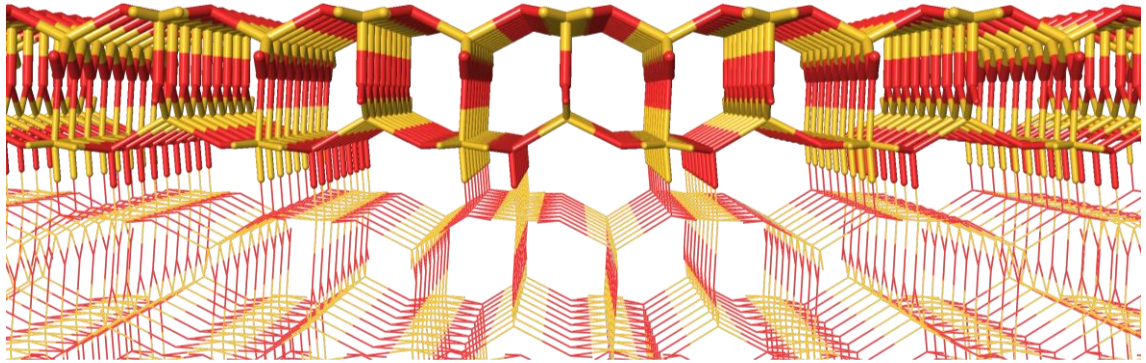
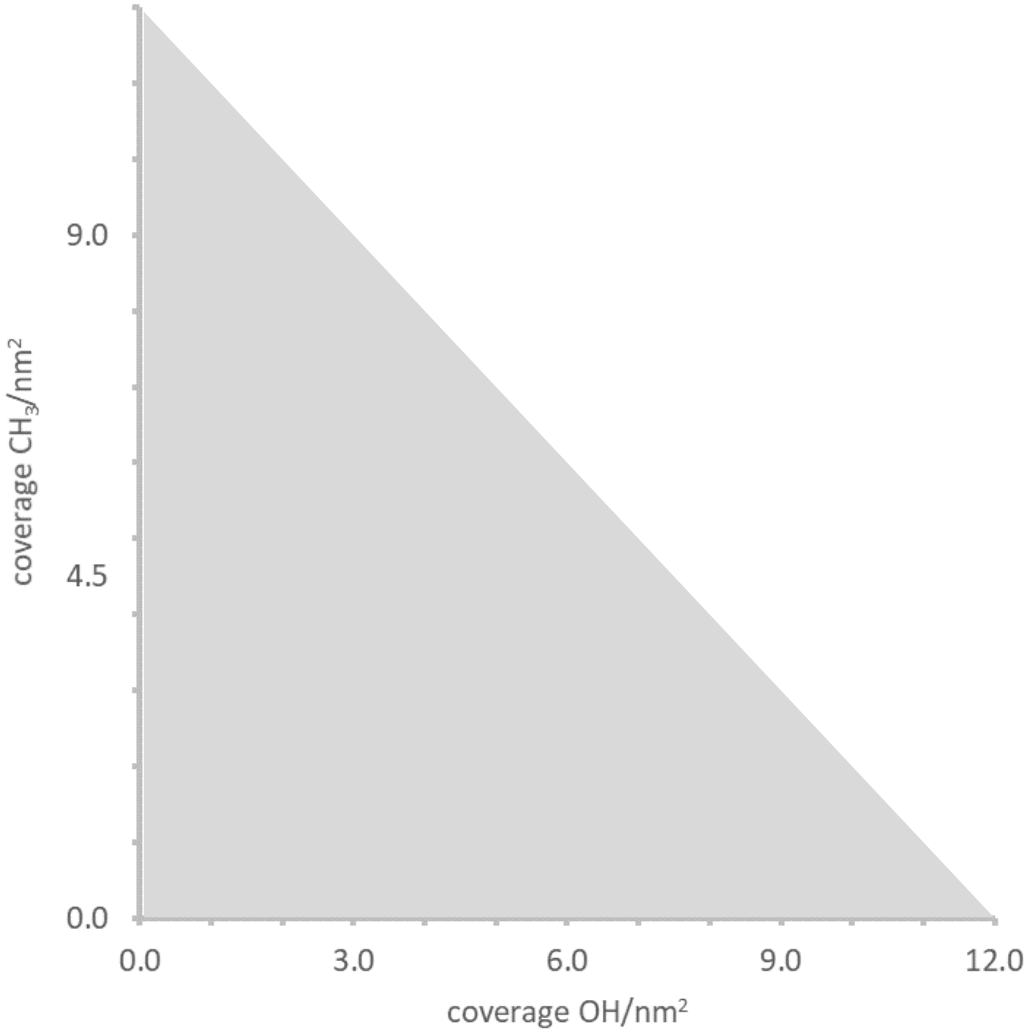


Chemical space of ALD



S. D. Elliott, Comp. Mater. Sci. 33, 20–25 (2005)

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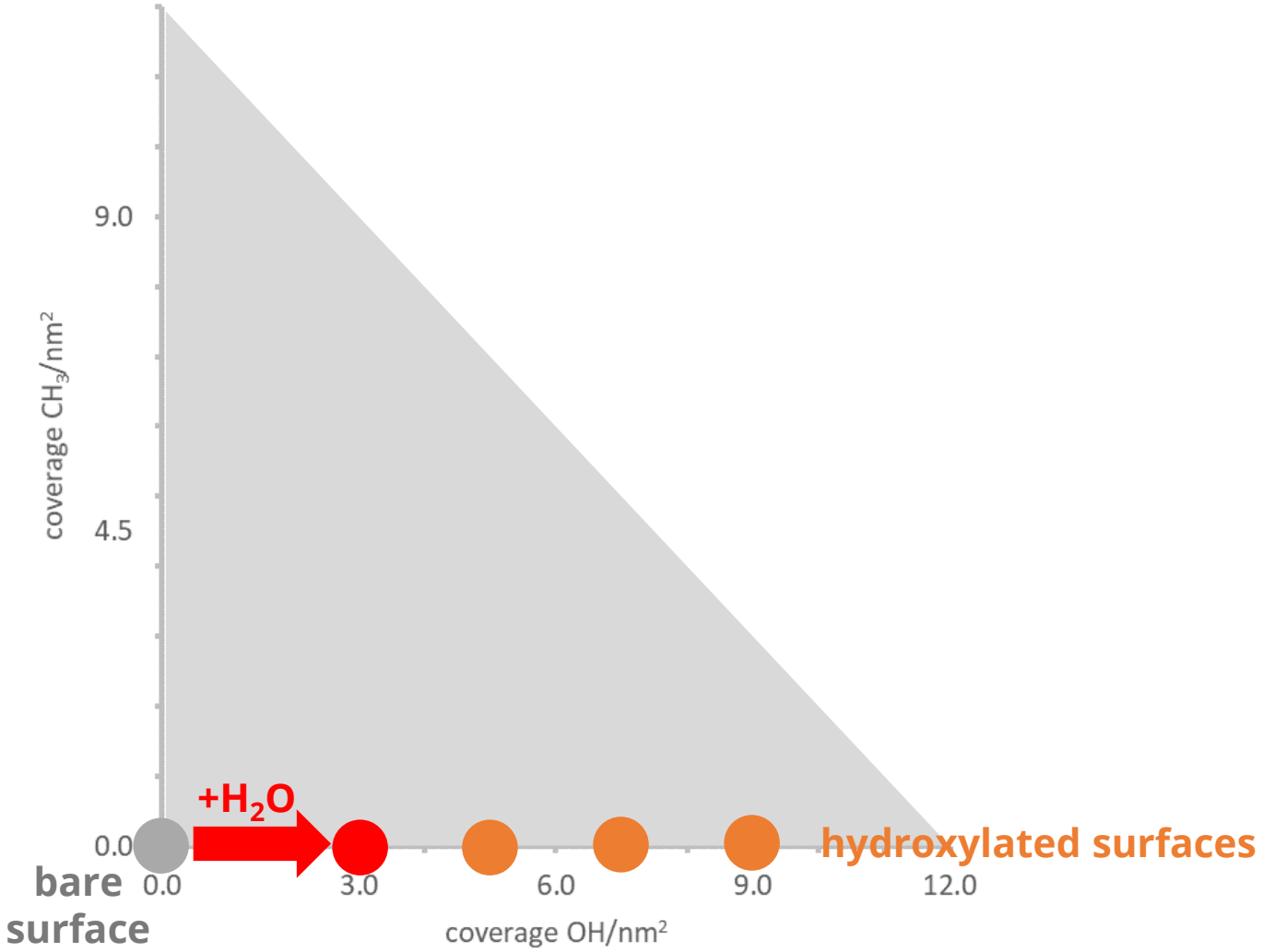

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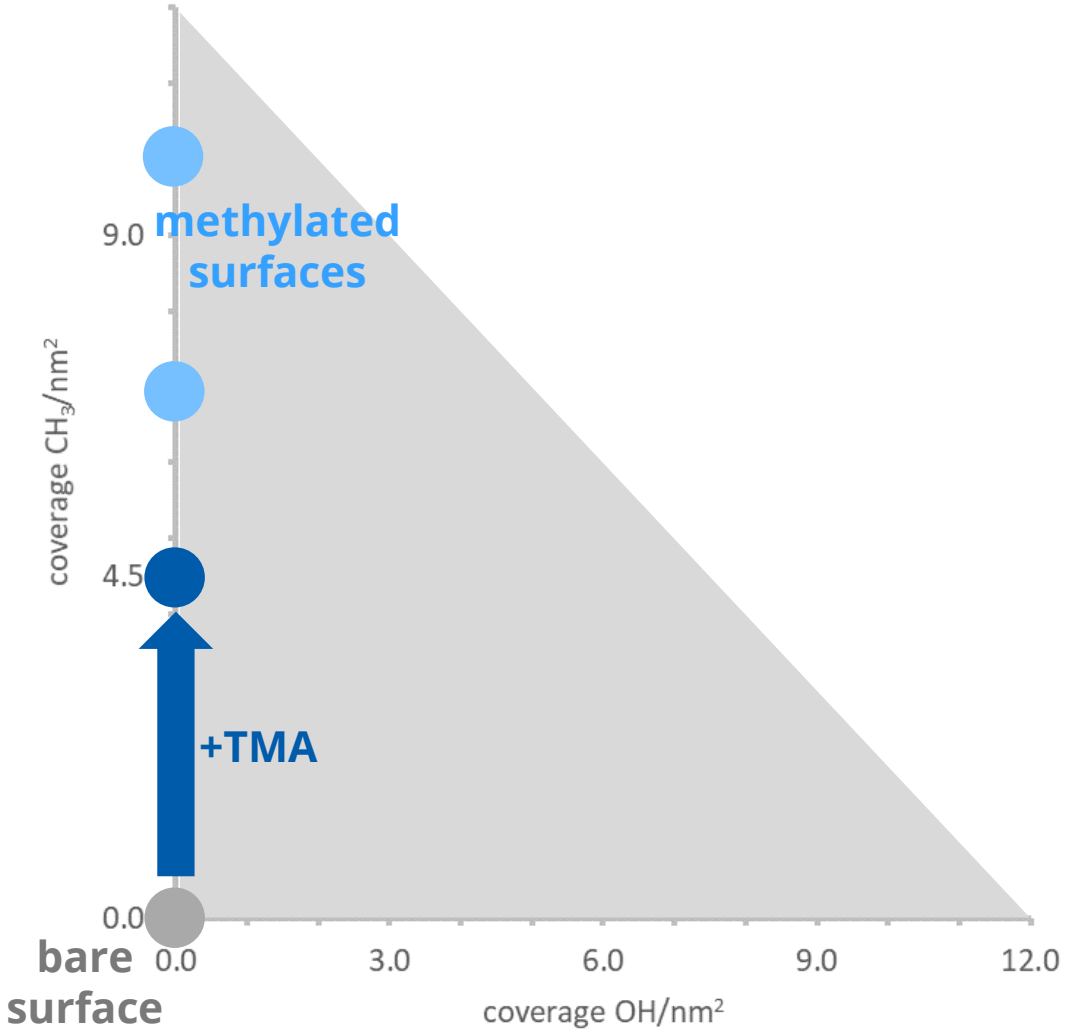

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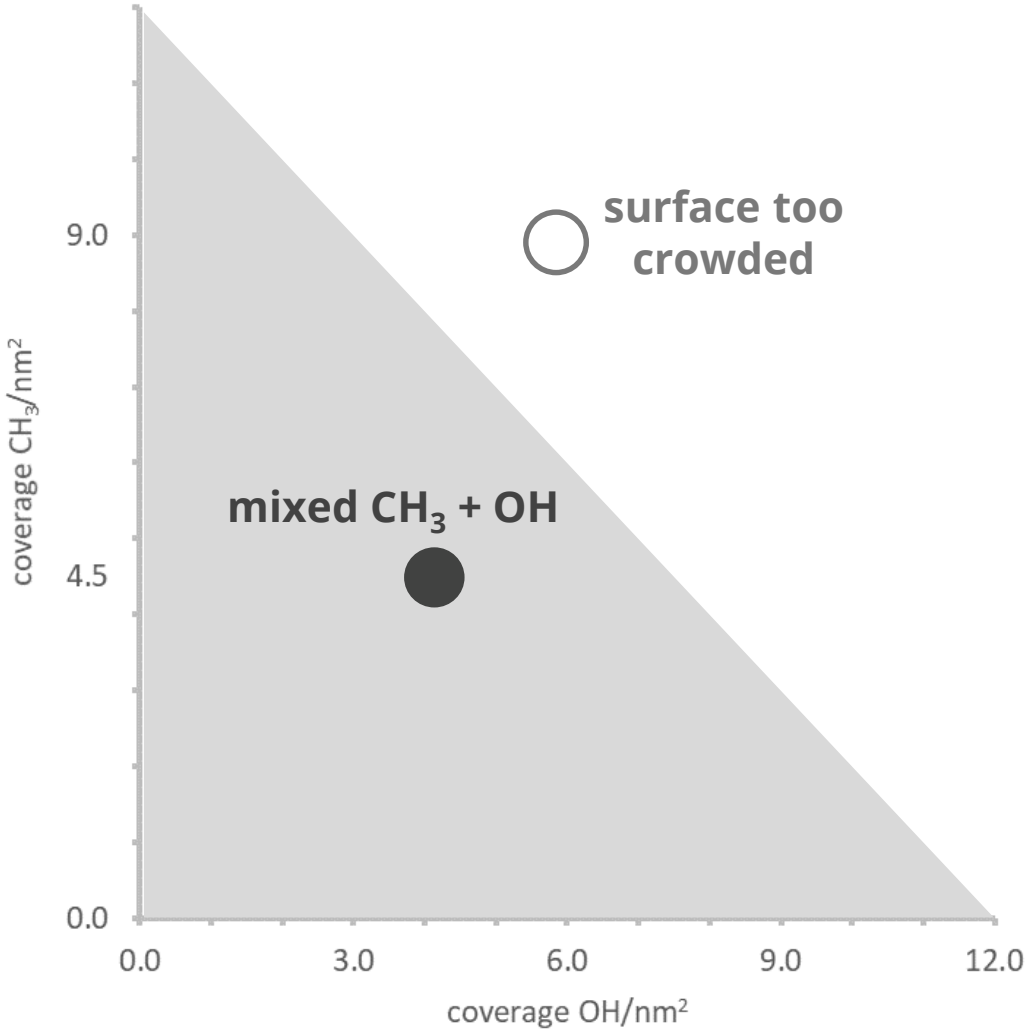

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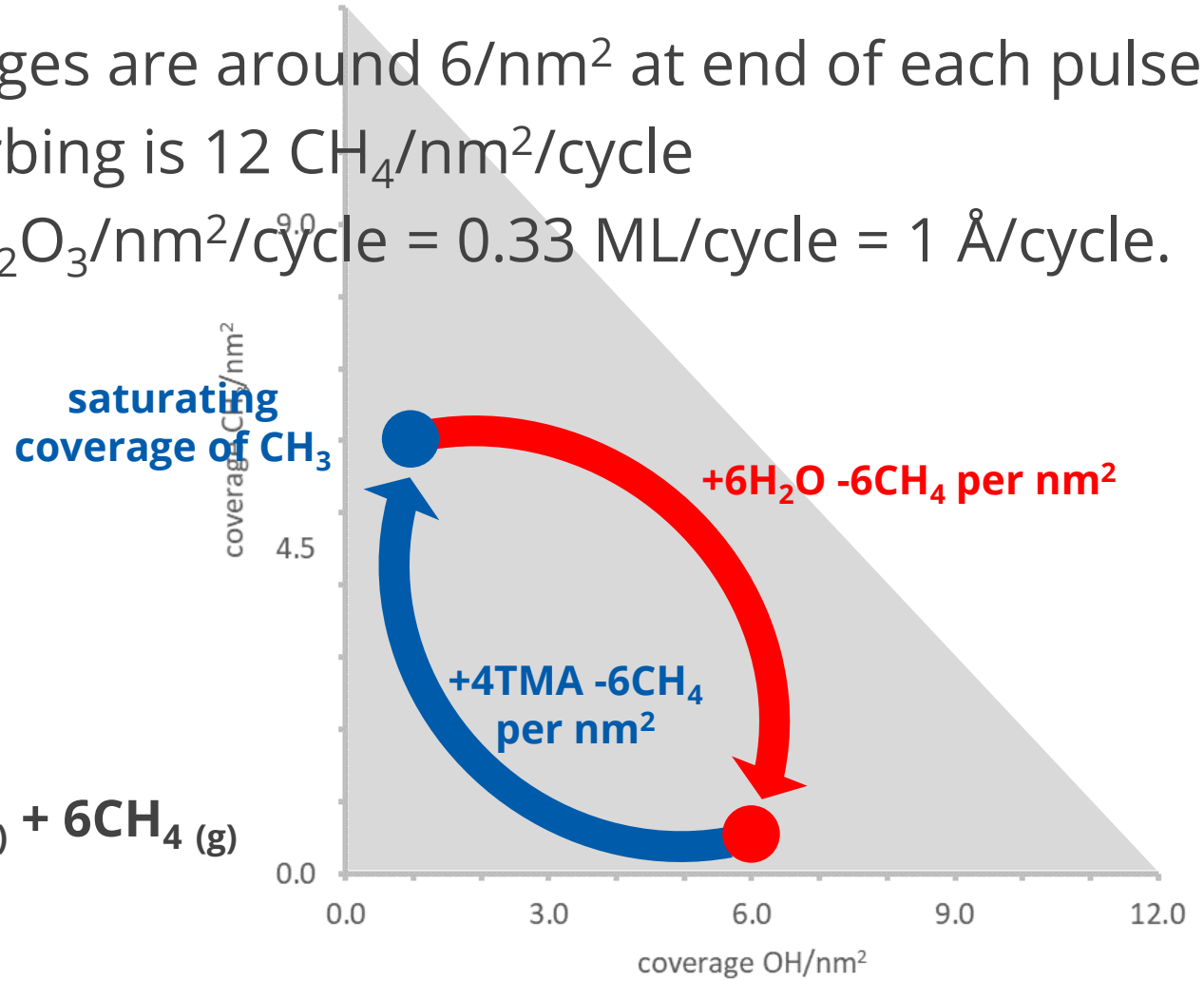
Chemical space of ALD

If both saturating coverages are around 6/nm^2 at end of each pulse

→ total by-product desorbing is 12 CH_4/nm^2/cycle

→ total deposition is 2 Al_2O_3/nm^2/cycle = 0.33 ML/cycle = 1 Å/cycle.



$2Al(CH_3)_{3\,(g)} + 3H_2O_{\,(g)} \rightarrow Al_2O_{3\,(s)} + 6CH_{4\,(g)}$

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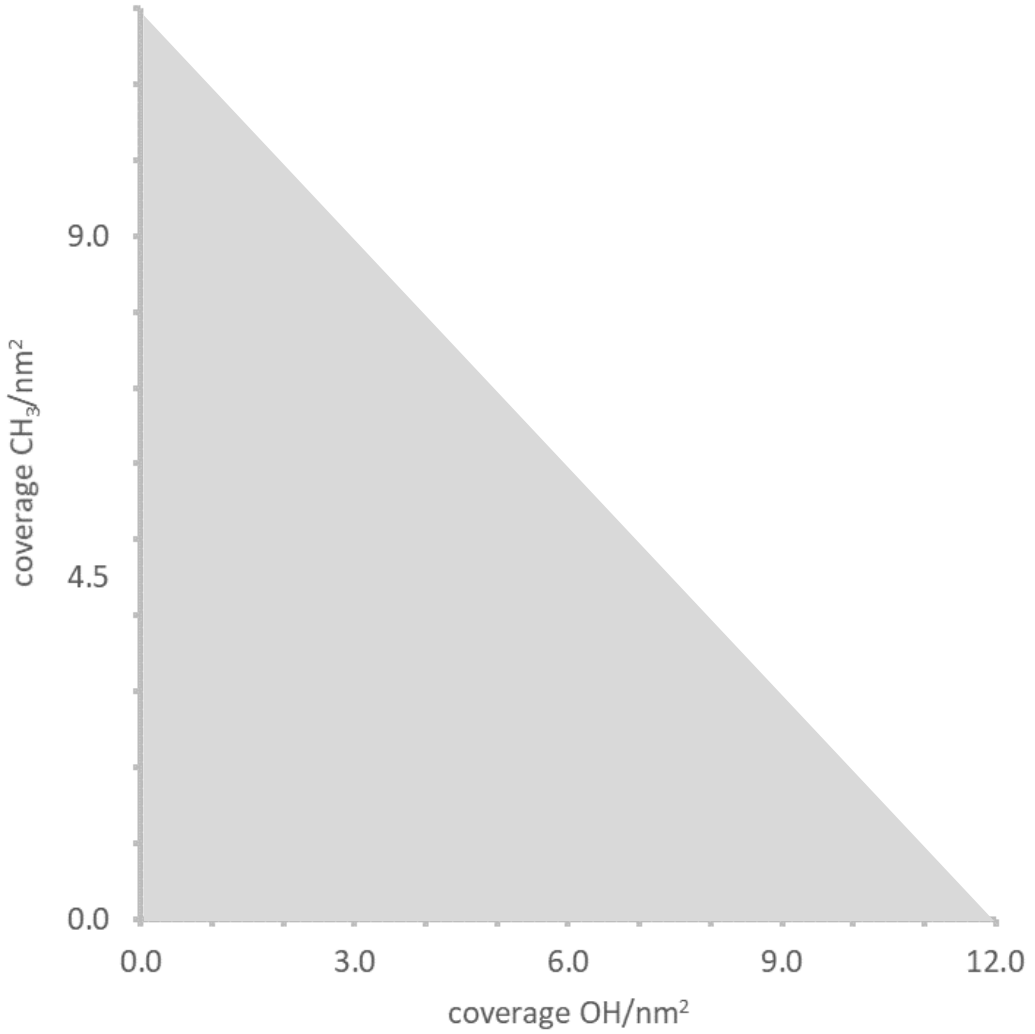
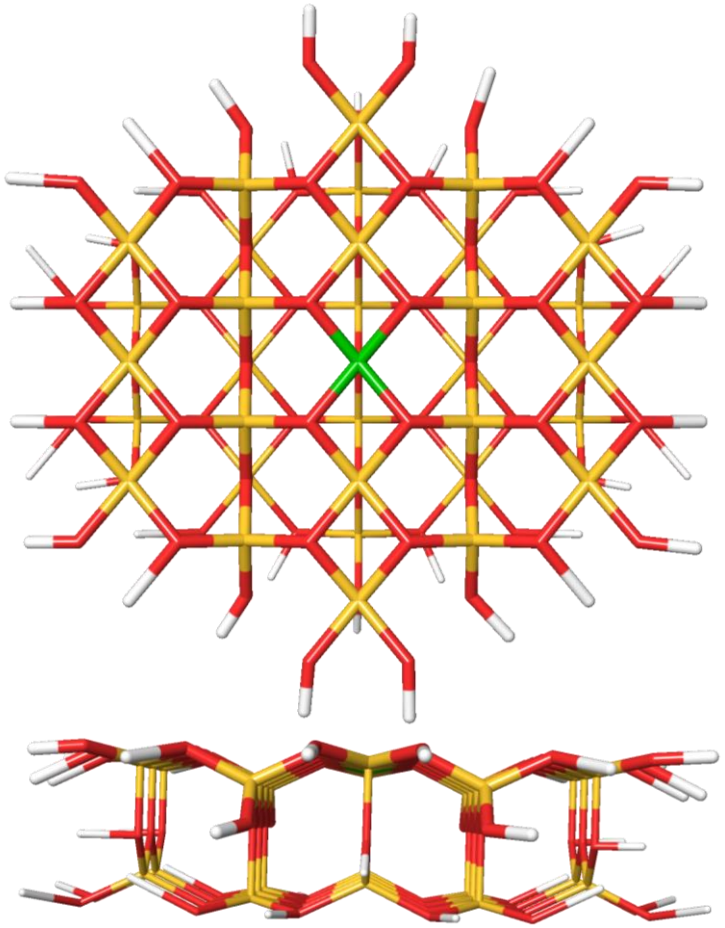
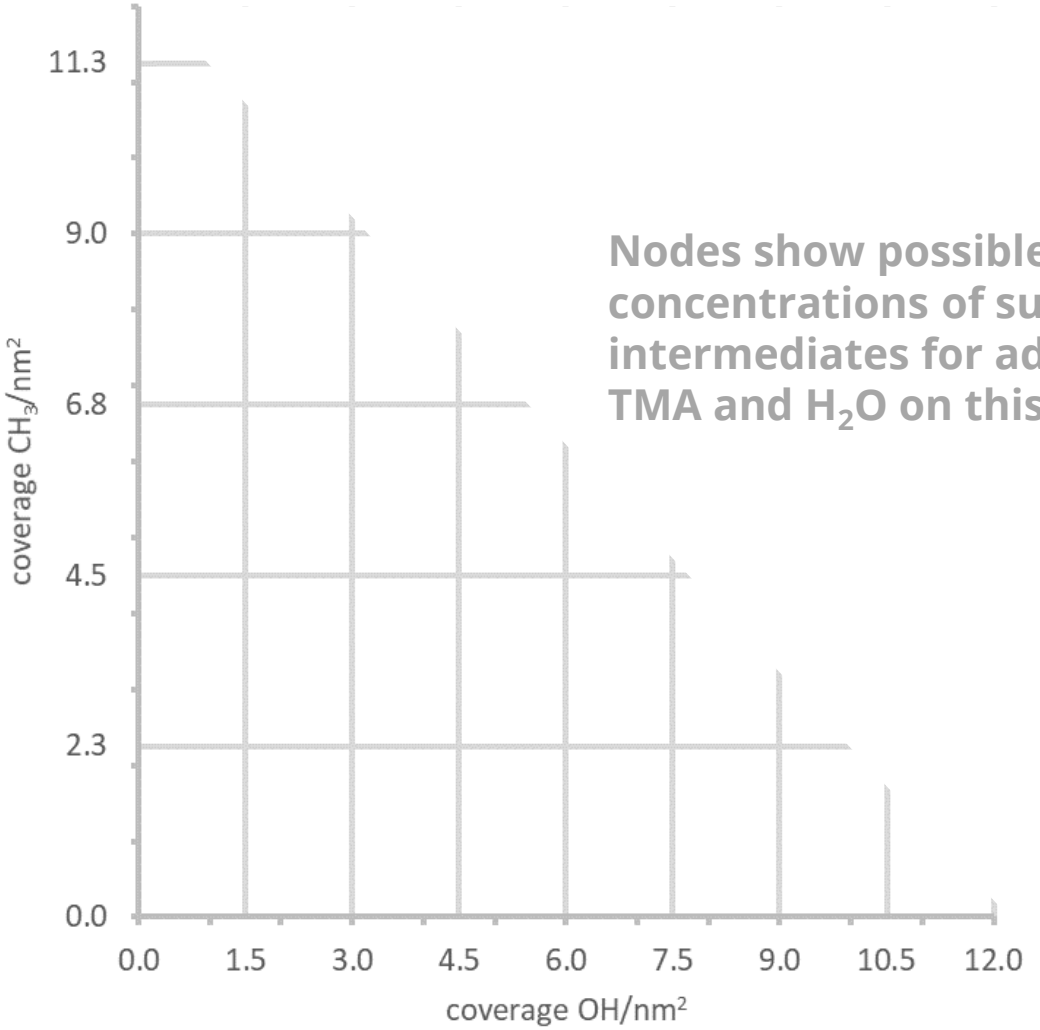
Chemical space of ALD



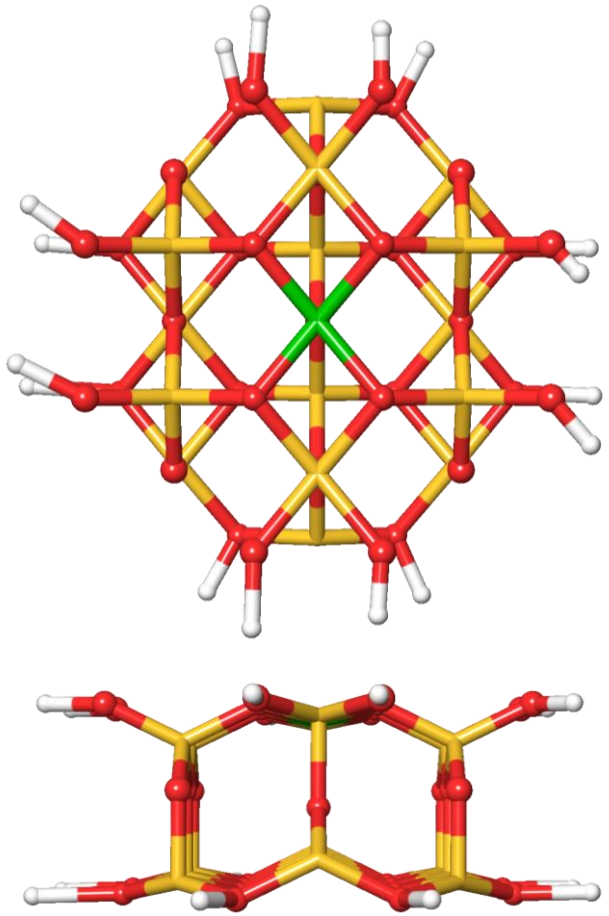
A model within the chemical space of ALD

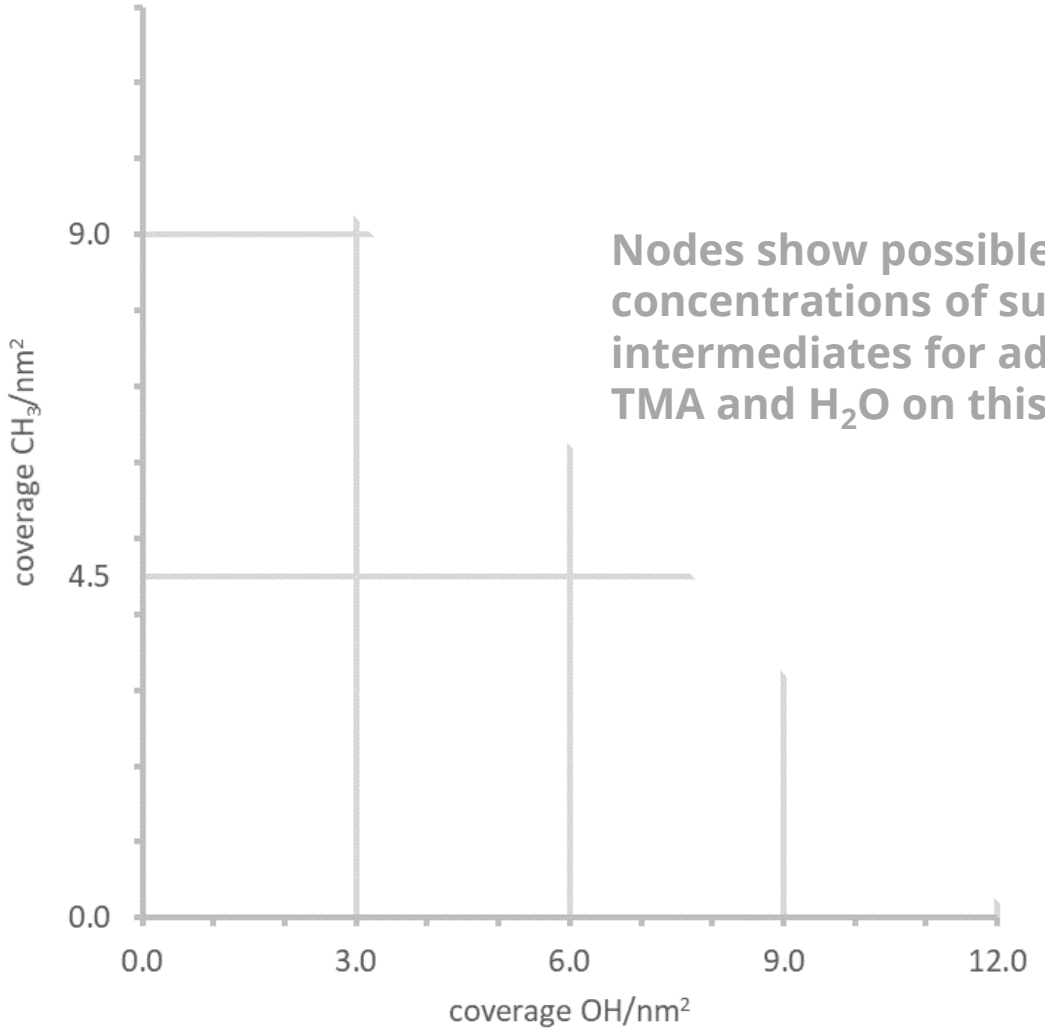




Nodes show possible concentrations of surface intermediates for adsorption of TMA and H_2O on this size of cluster

A model within the chemical space of ALD





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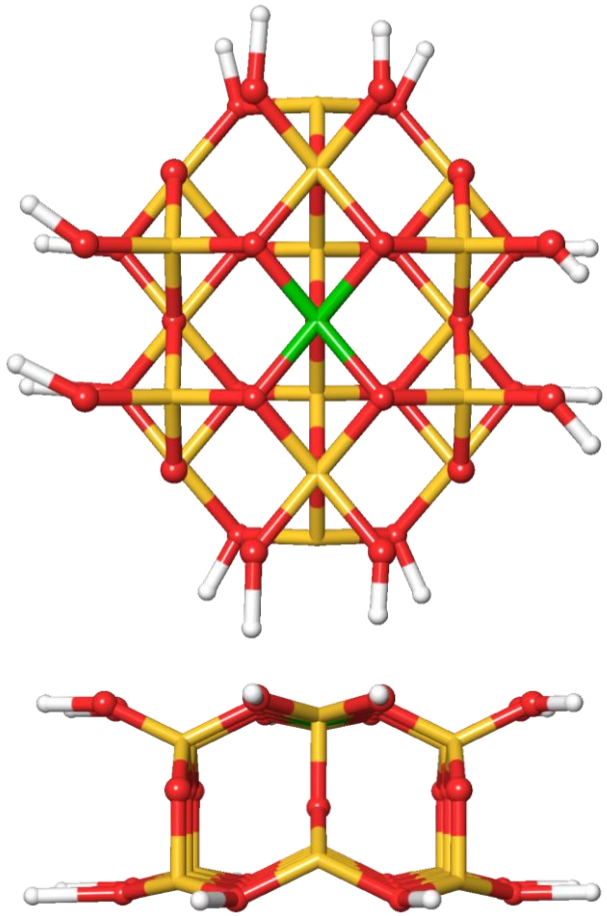

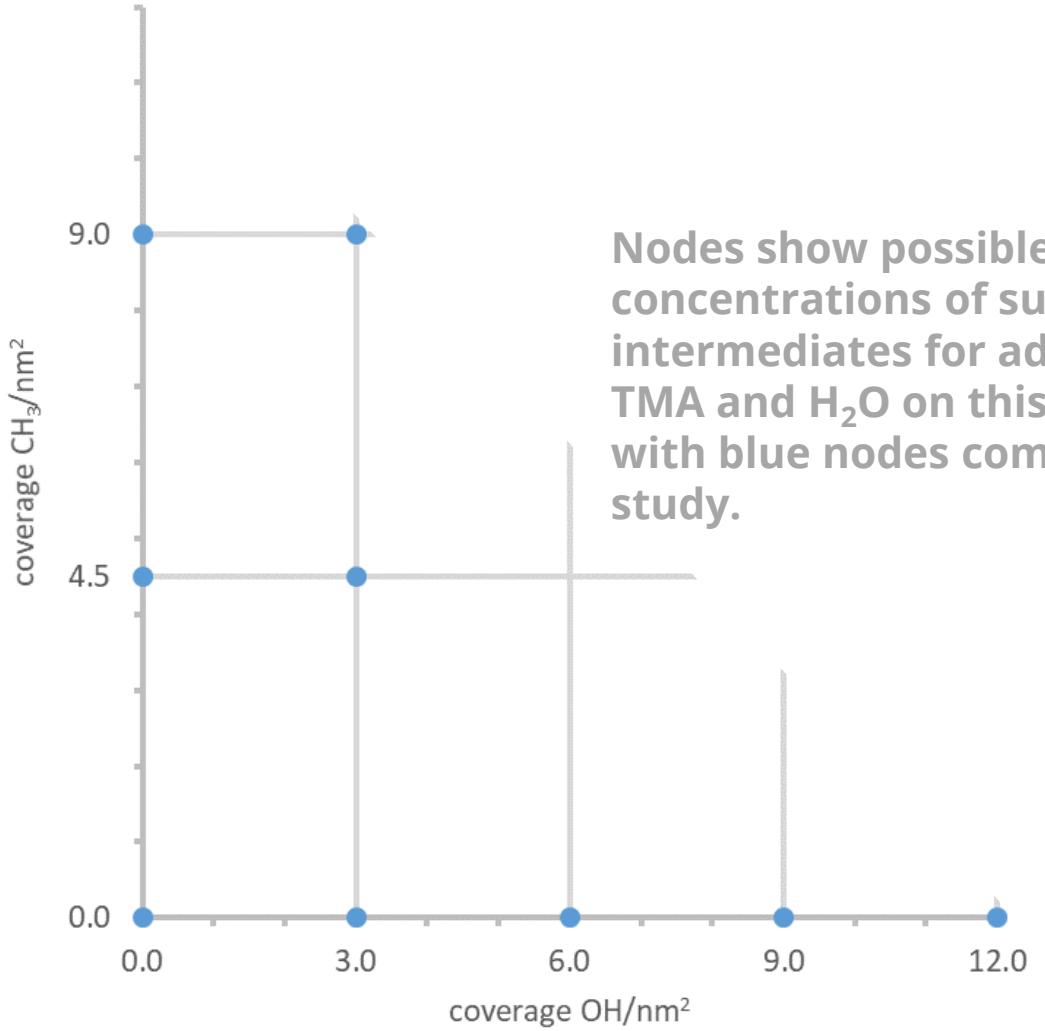

Nodes show possible concentrations of surface intermediates for adsorption of TMA and H_2O on this size of cluster, with blue nodes computed in this study.

Enumeration of structures for H_2O adsorption

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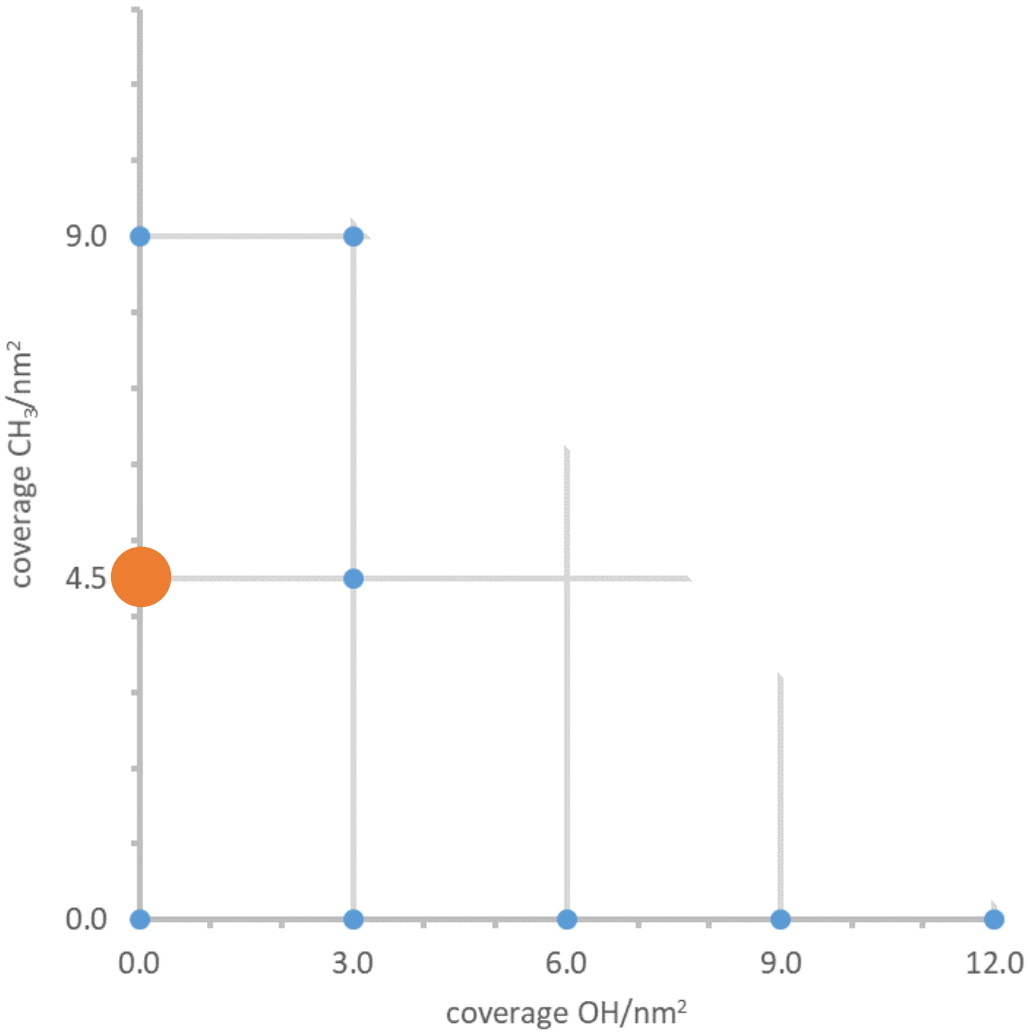
Adsorption of H_2O onto methylated surface



APPROACH:

- At each surface concentration, systematically enumerate all symmetry-distinct isomers:
  - 24 isomers across range of methyl concentrations
  - 24 isomers across range of hydroxyl coverages.
- Optimize those structures at DFT level (B3LYP-D3/LACVP*) and select valid structures.
- Add H_2O adsorbate to chosen site and reoptimize with DFT.
- Optimizations each take 50-70 cpu-hours; total time 110 cpu-days.

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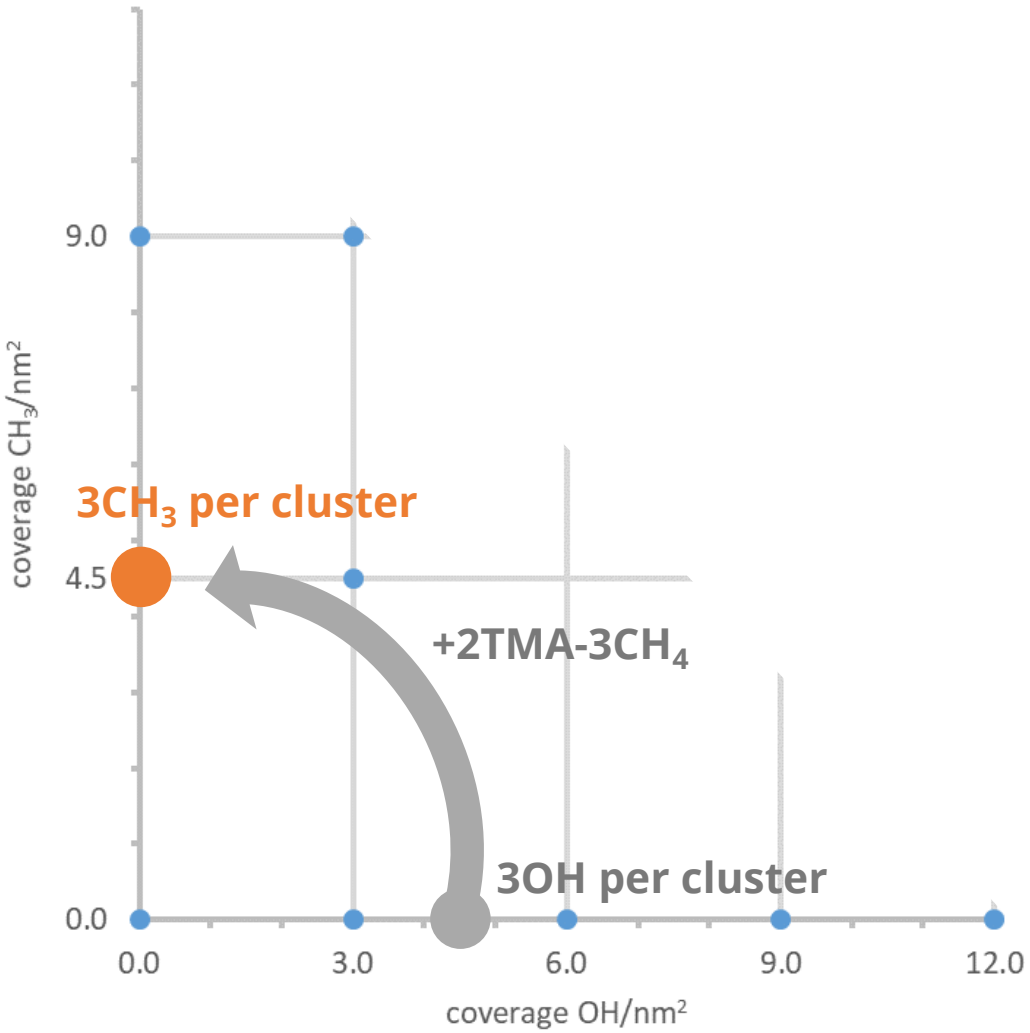

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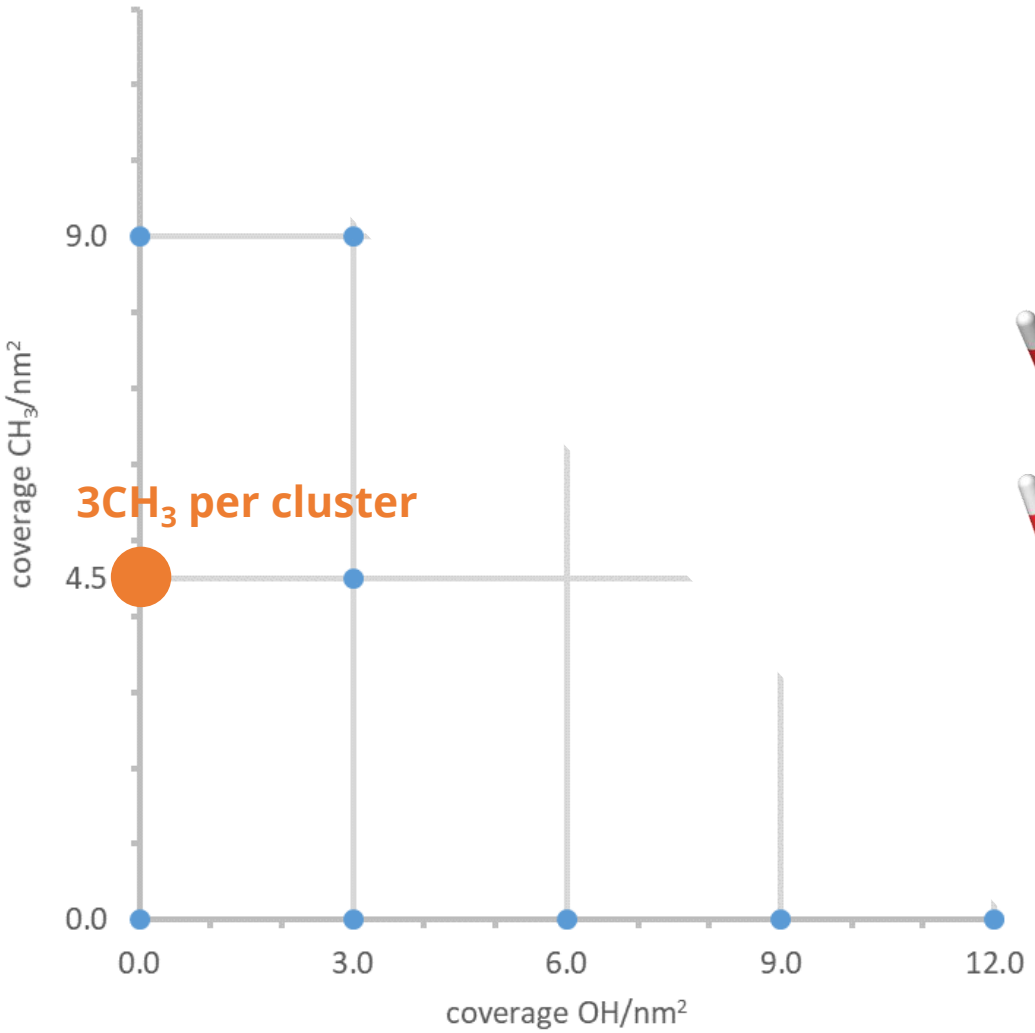
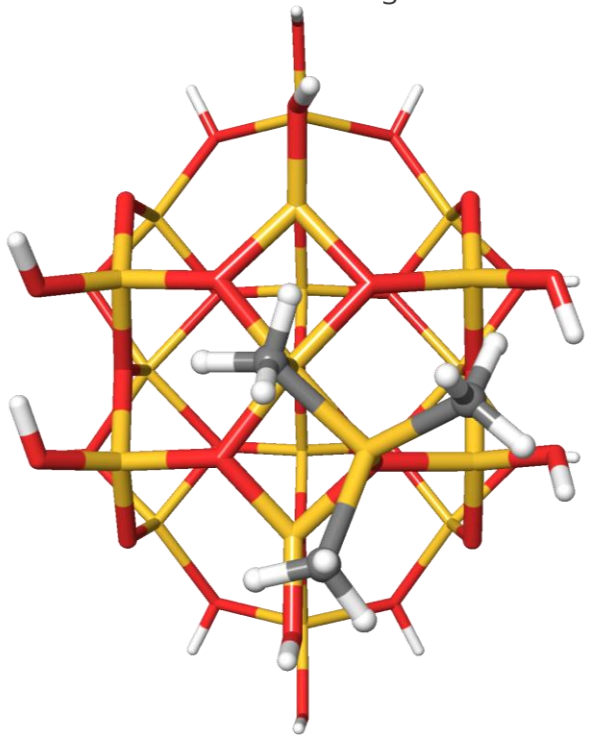


most stable isomer
with $3CH_3$



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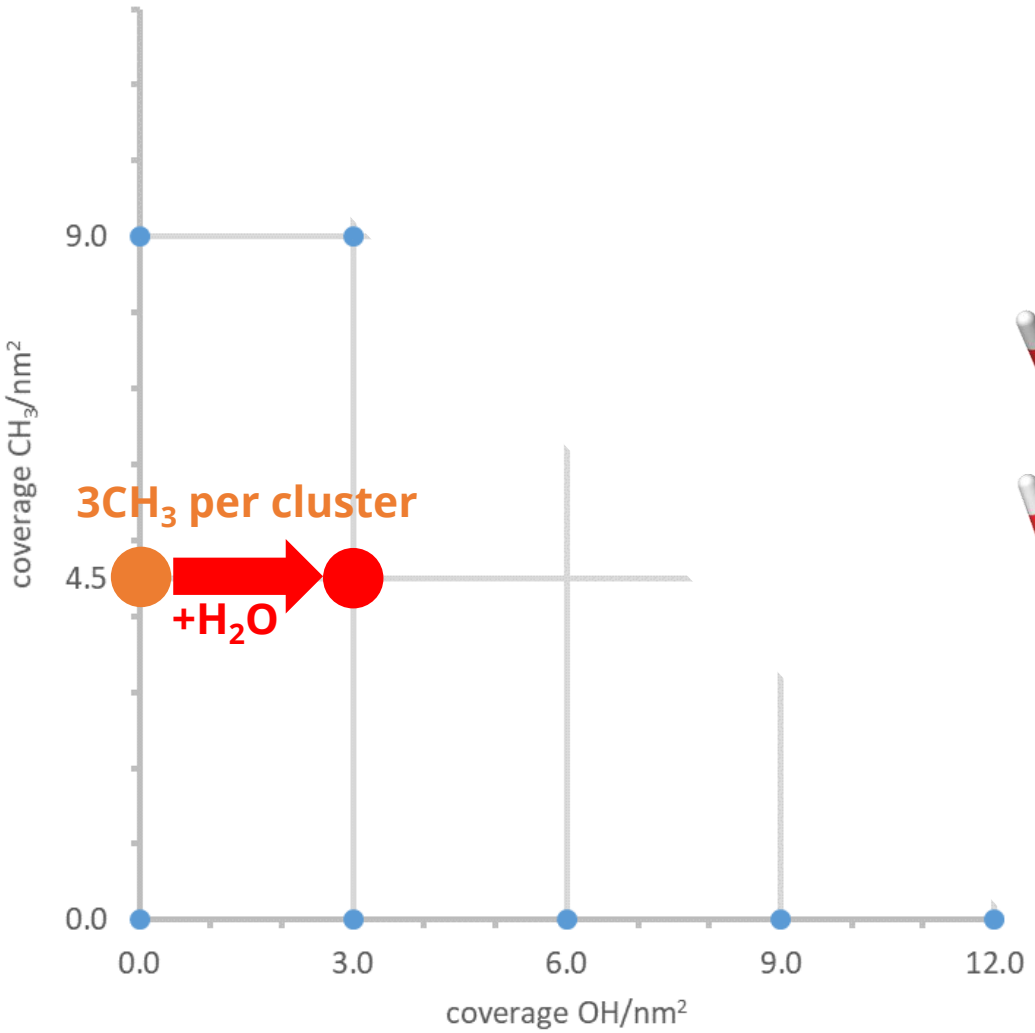

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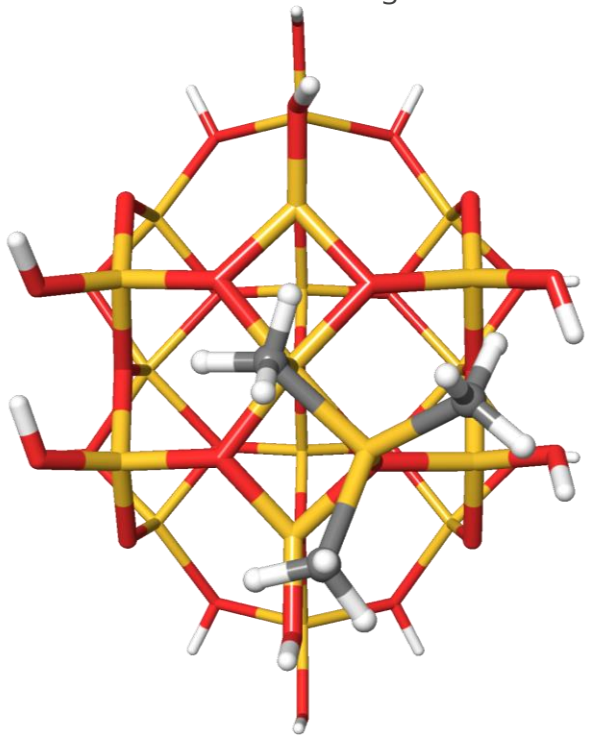
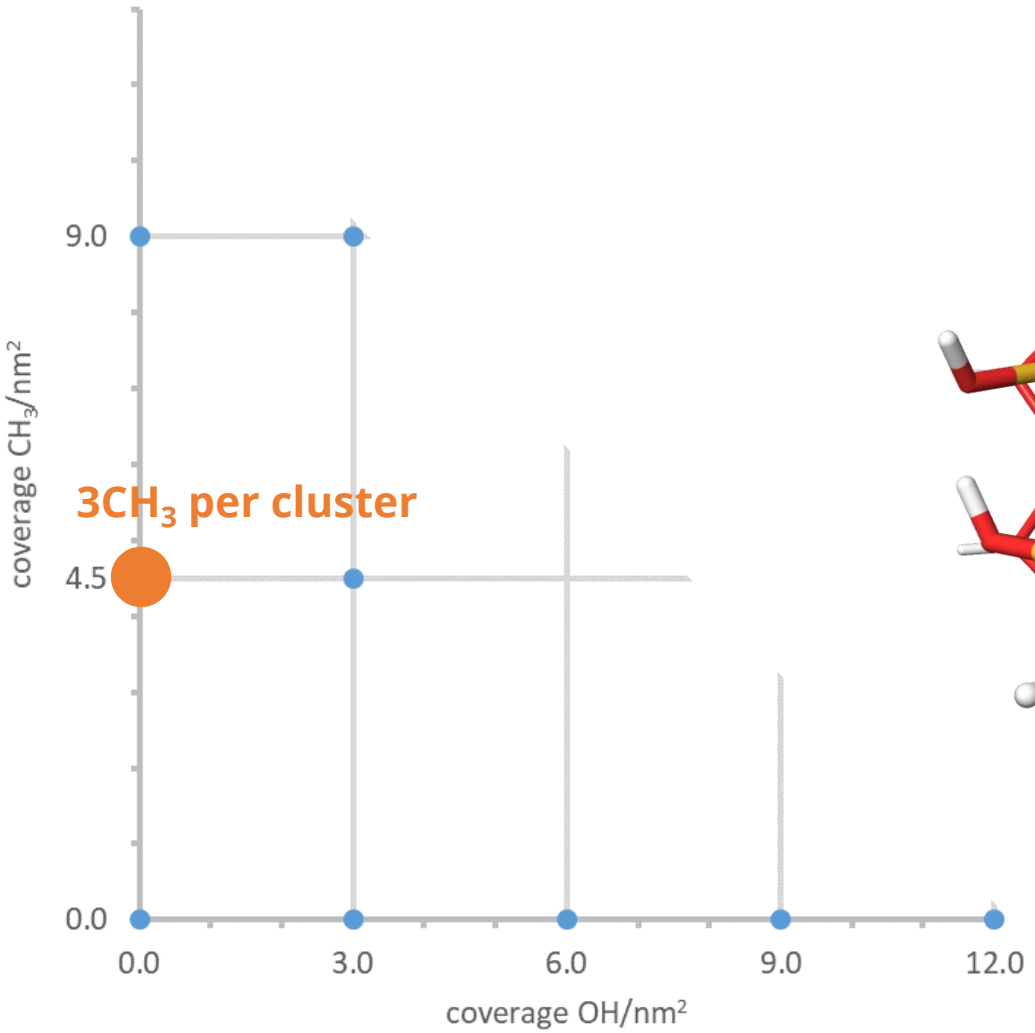
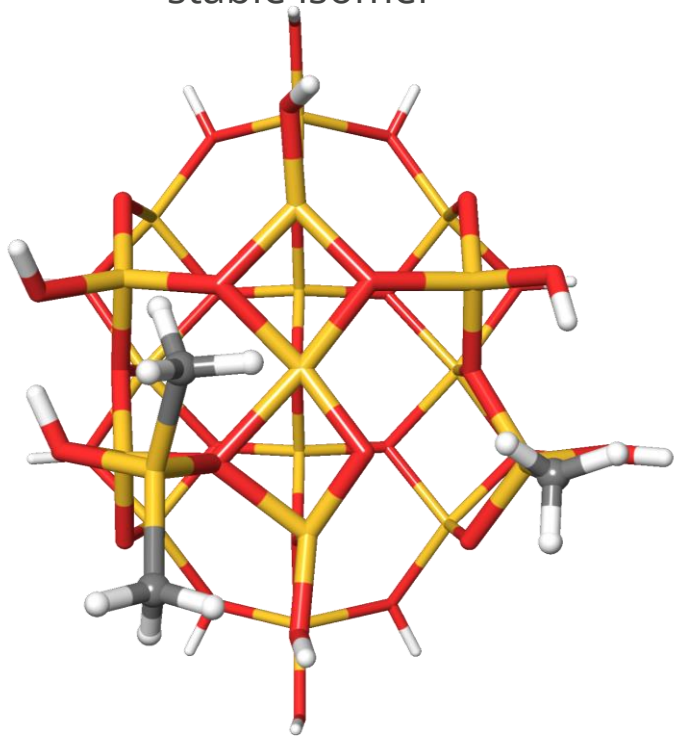


→ adsorption site for H_2O is already occupied

Adsorption of H_2O onto methylated surface

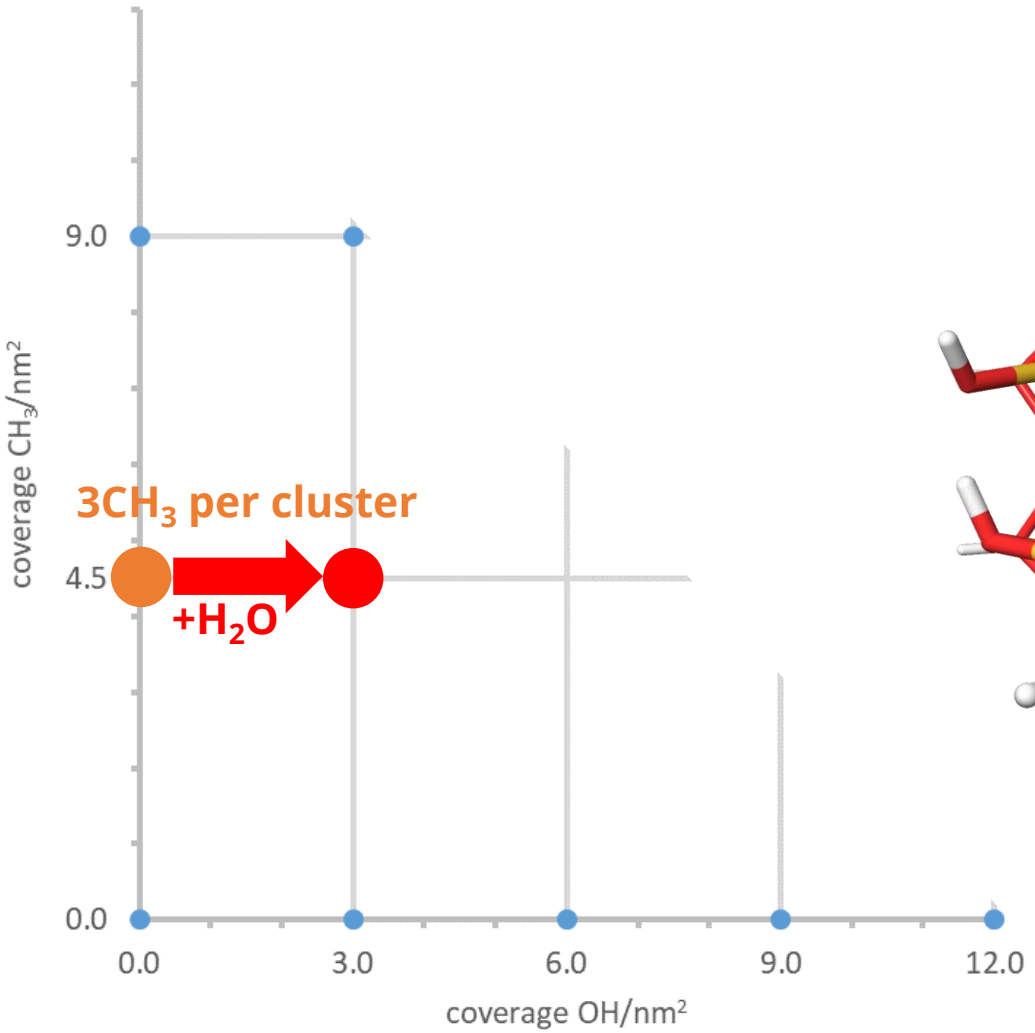


27.2 kJ/mol less stable isomer



DFT-computed Gibbs free energies at 200°C and 1 atm, $T\Delta S(H_2O)$=89.4 kJ/mol

Adsorption of H_2O onto methylated surface



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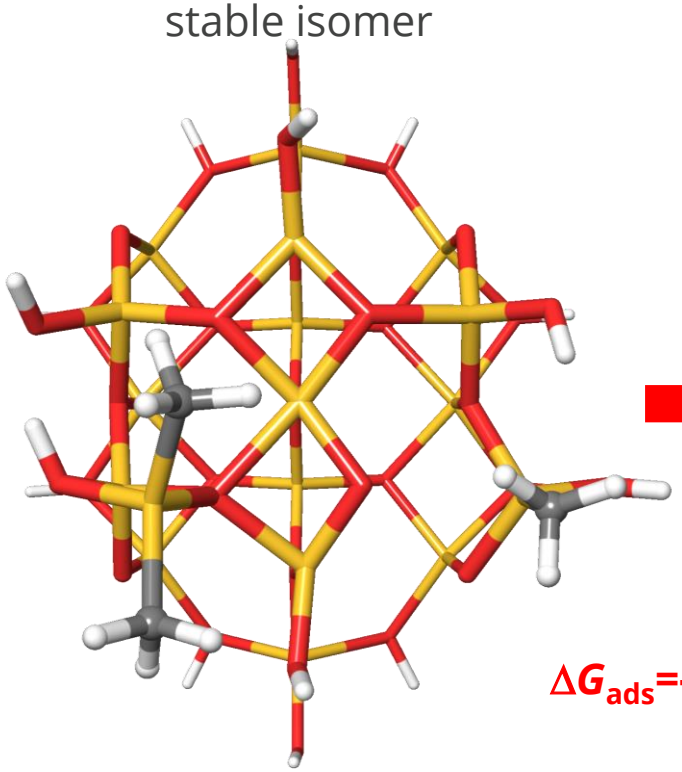
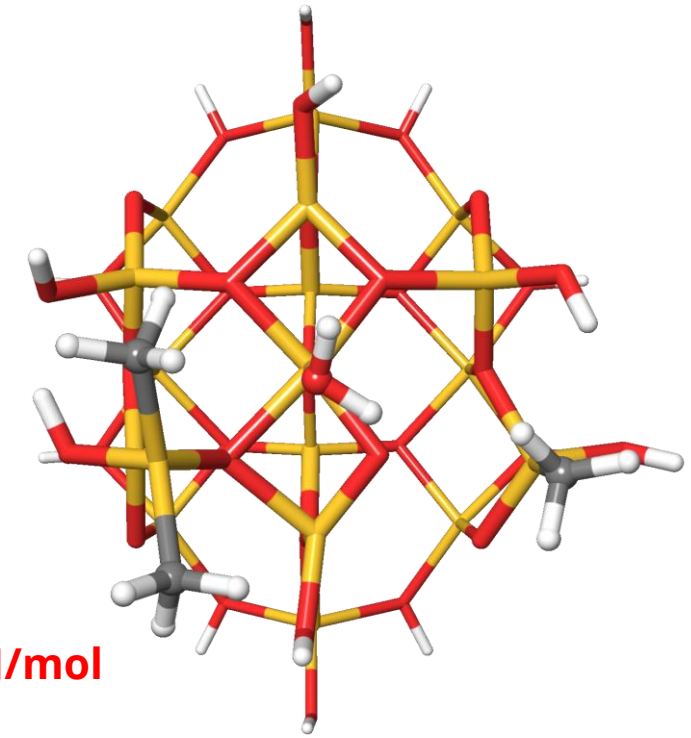
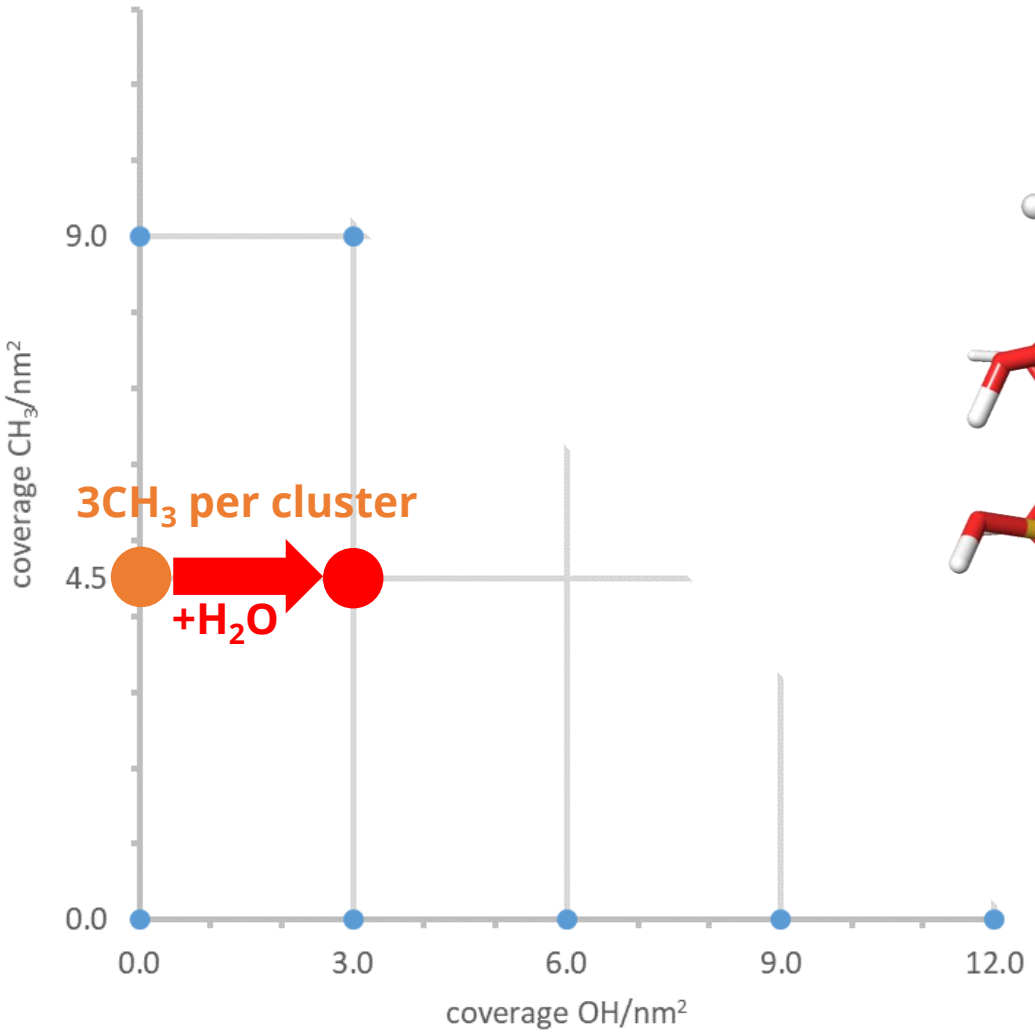




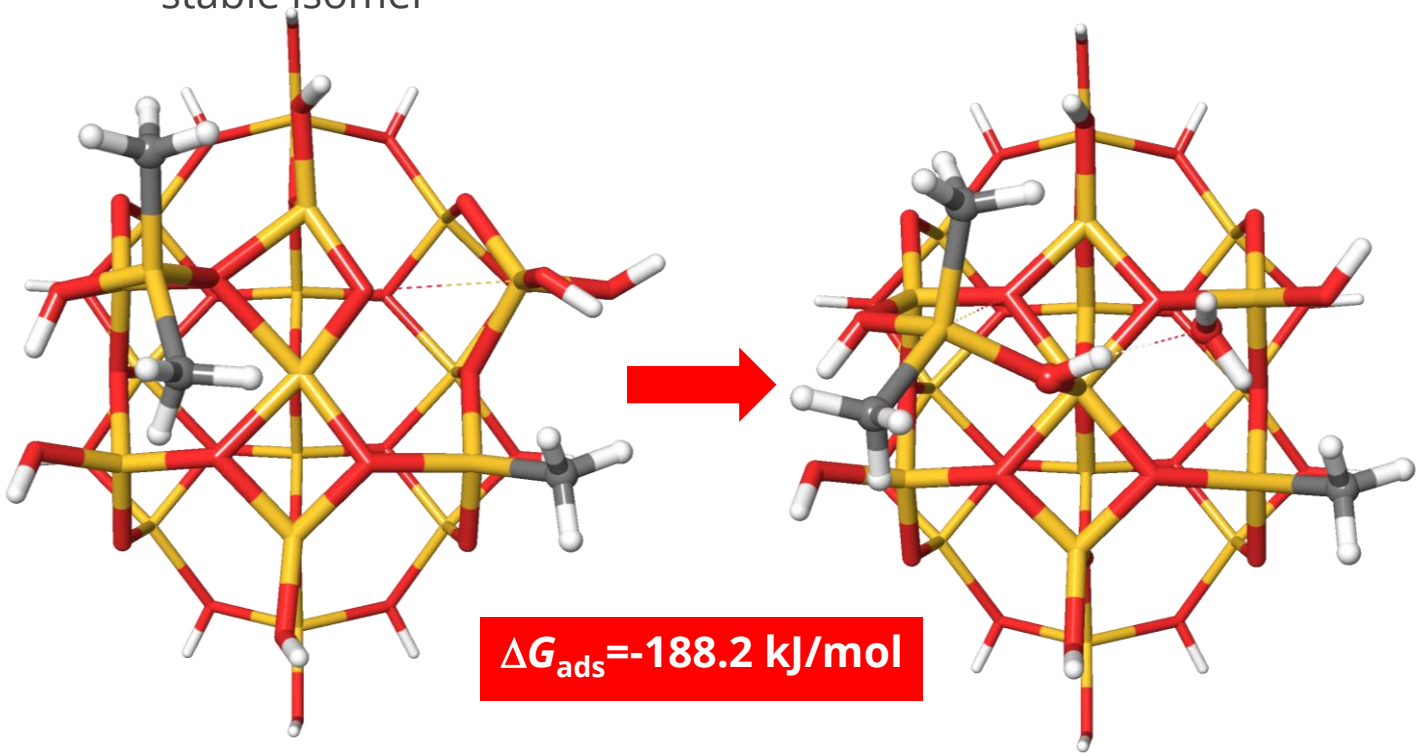
ΔG_{ads}=-27.9 kJ/mol

DFT-computed Gibbs free energies at 200°C and 1 atm, $T\Delta S(H_2O)$=89.4 kJ/mol

Adsorption of H_2O onto methylated surface



31.9 kJ/mol less stable isomer

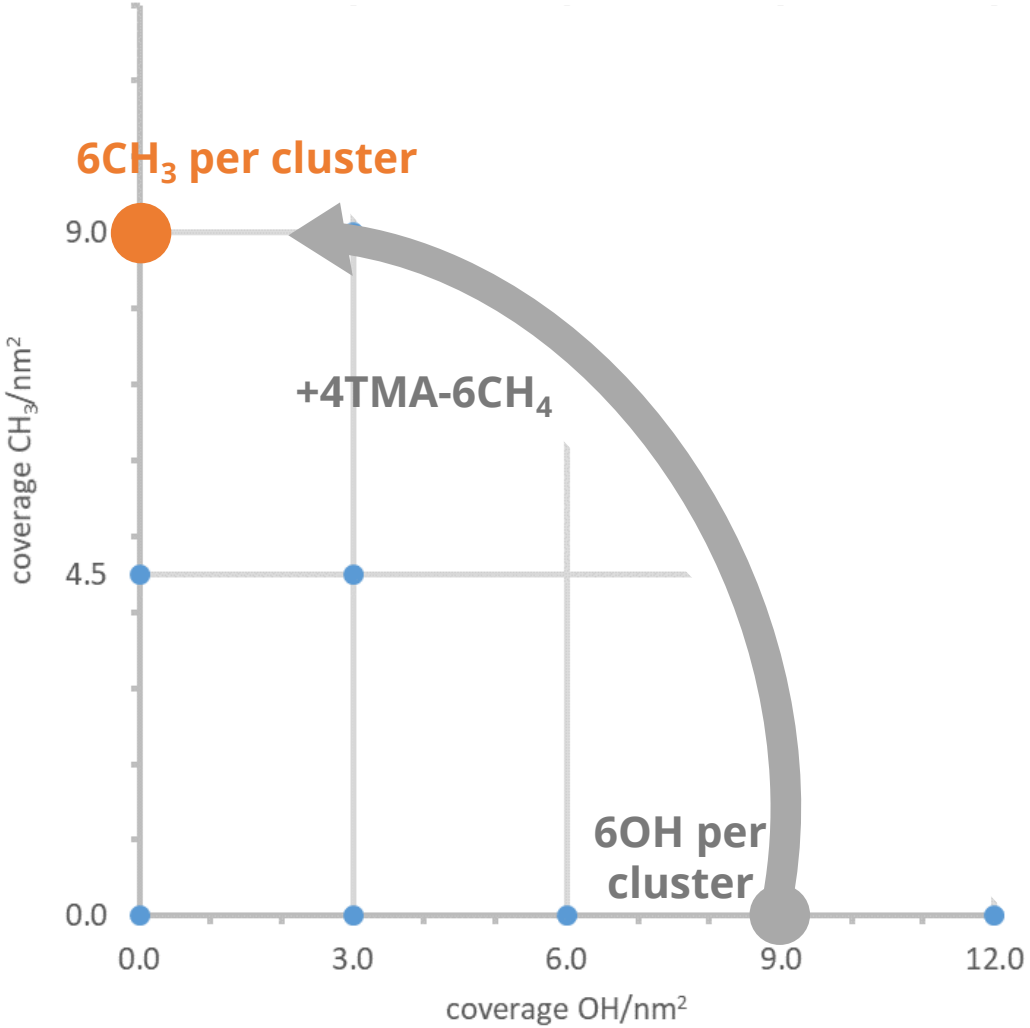


ΔG_{ads}=-188.2 kJ/mol

Need to check outliers like this one – they may flag up a different category of chemistry.

DFT-computed Gibbs free energies at 200°C and 1 atm, $T\Delta S(H_2O)$=89.4 kJ/mol

Adsorption of H_2O onto methylated surface



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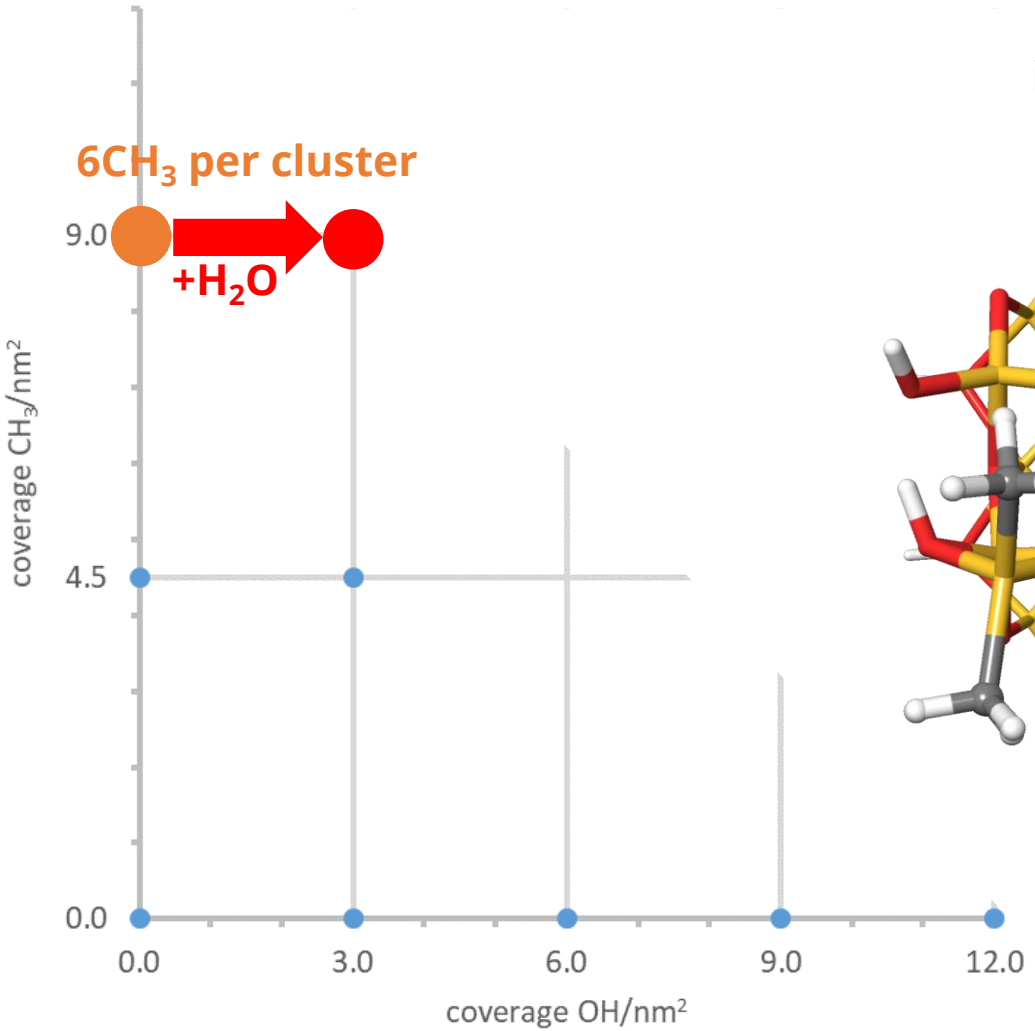
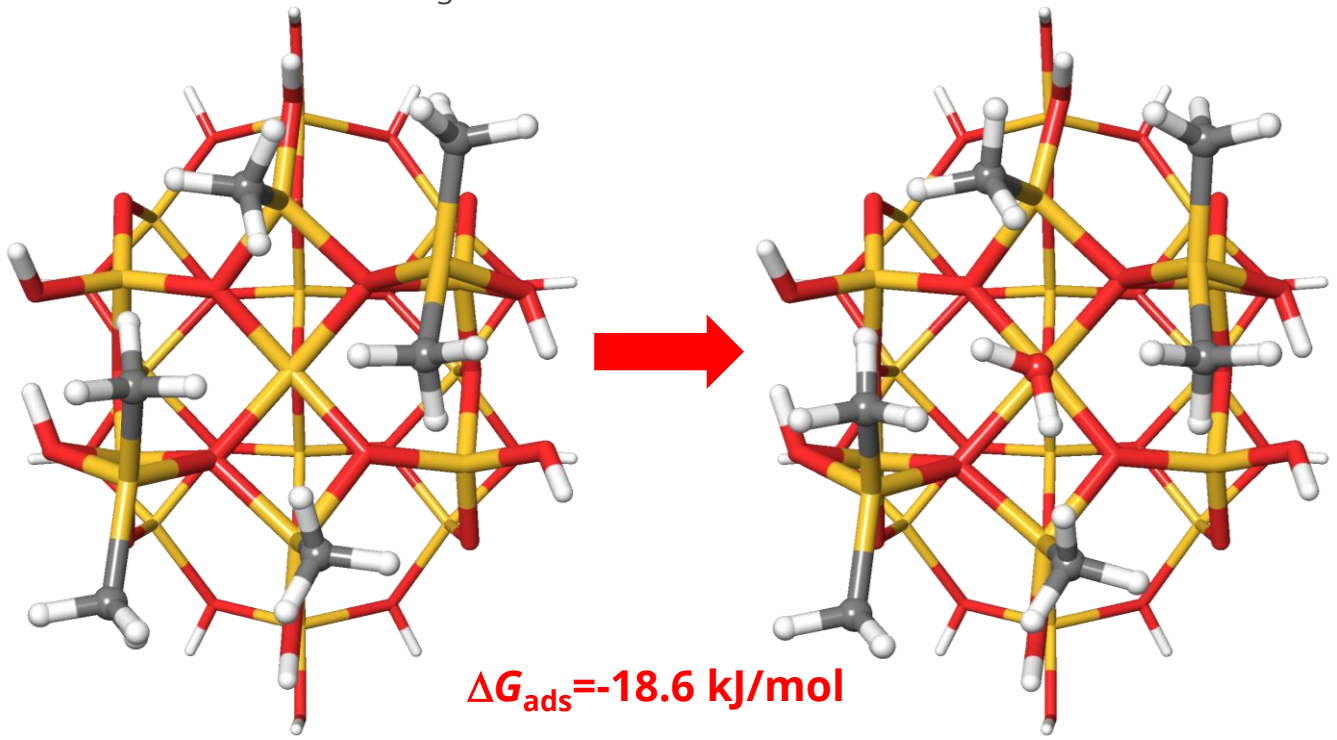


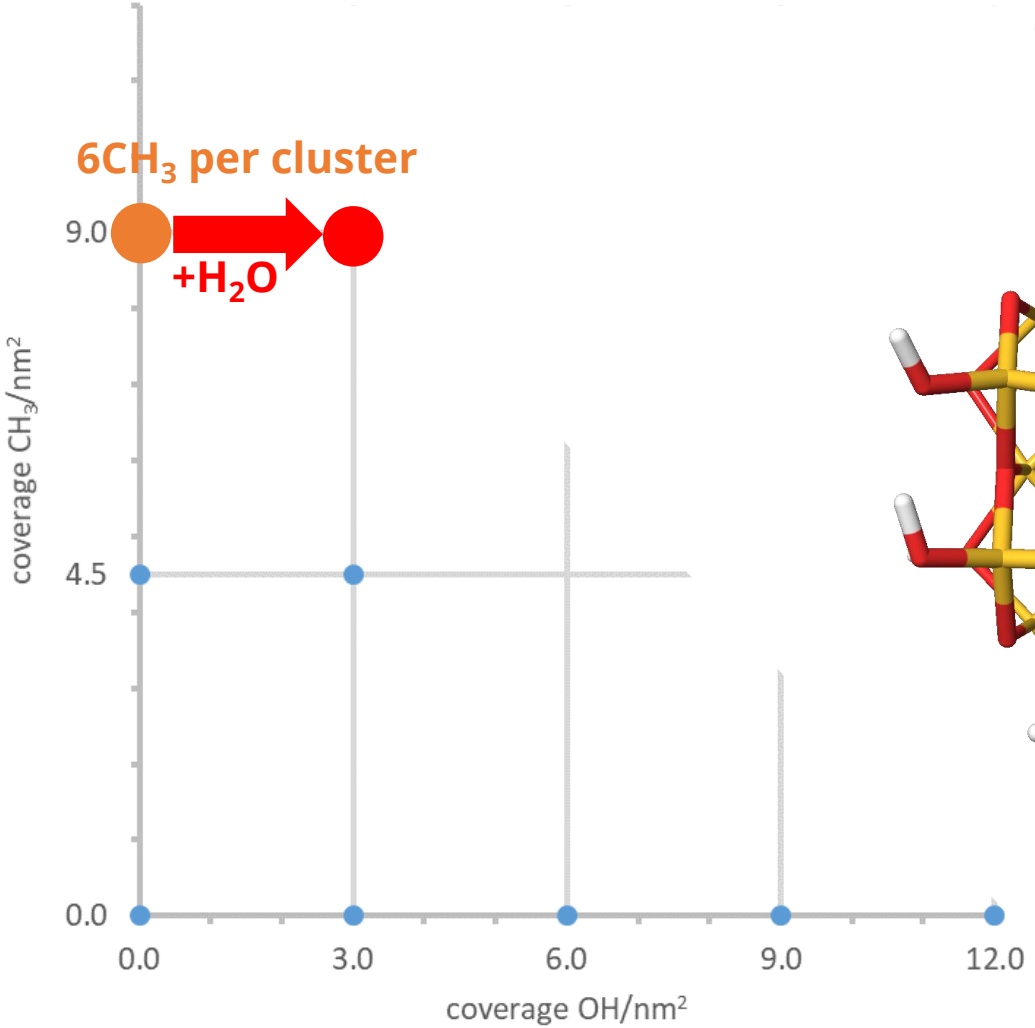
most stable isomer at $6CH_3$



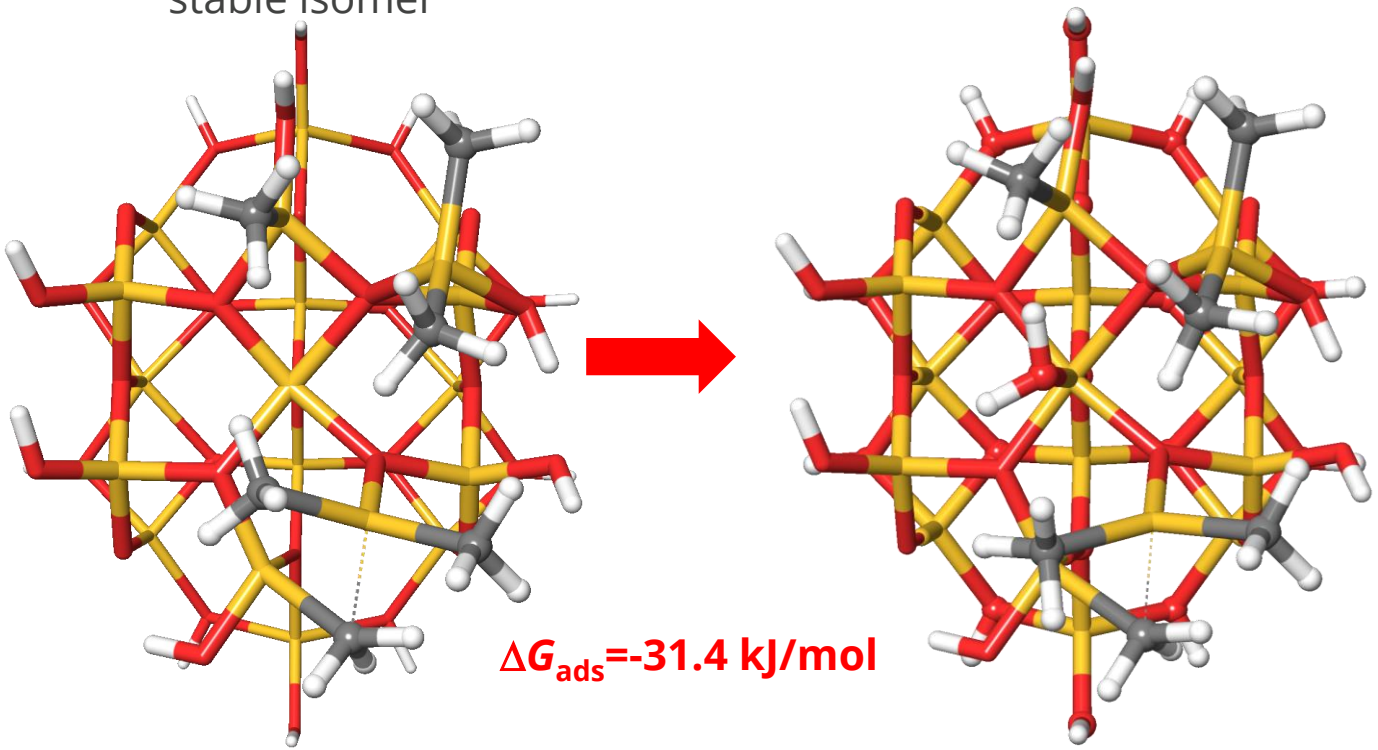
ΔG_{ads}=-18.6 kJ/mol

DFT-computed Gibbs free energies at 200°C and 1 atm, $T\Delta S(H_2O)$=89.4 kJ/mol

Adsorption of H_2O onto methylated surface



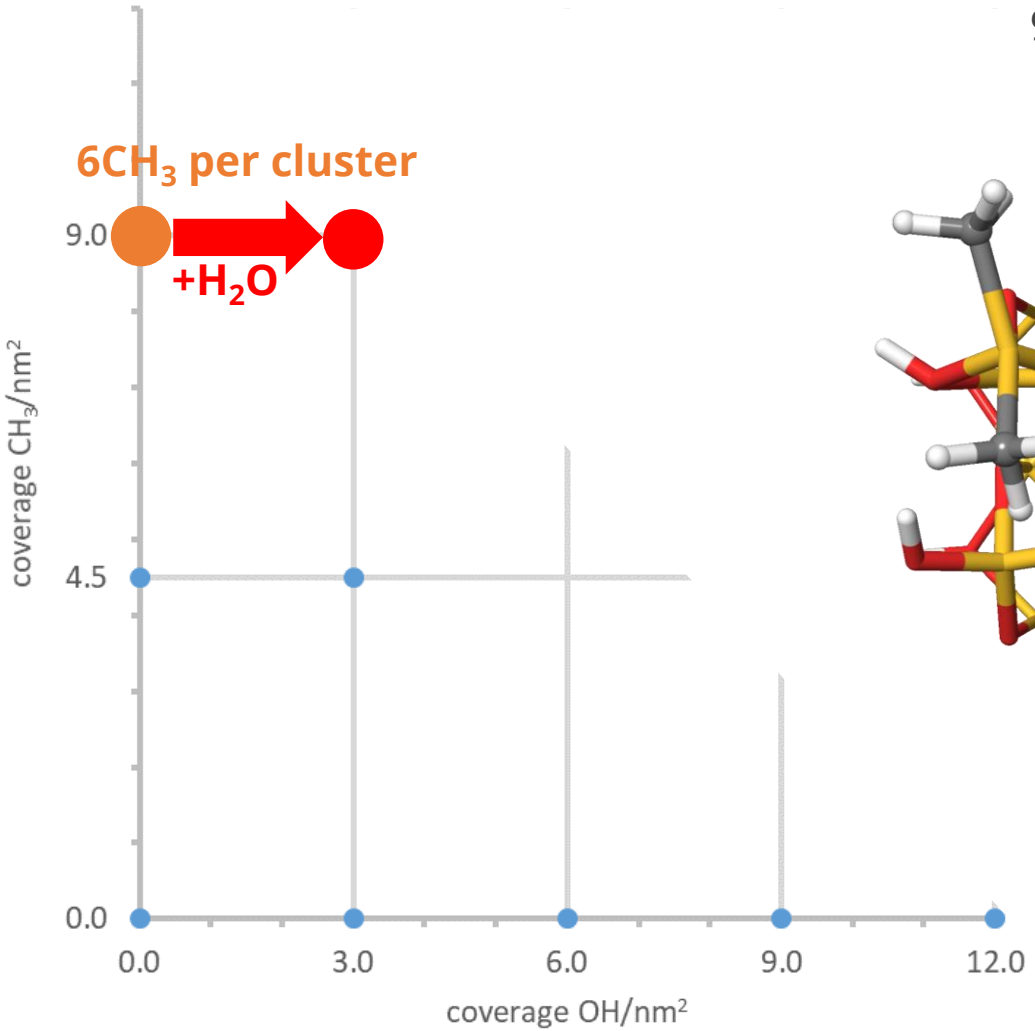
91.3 kJ/mol less stable isomer



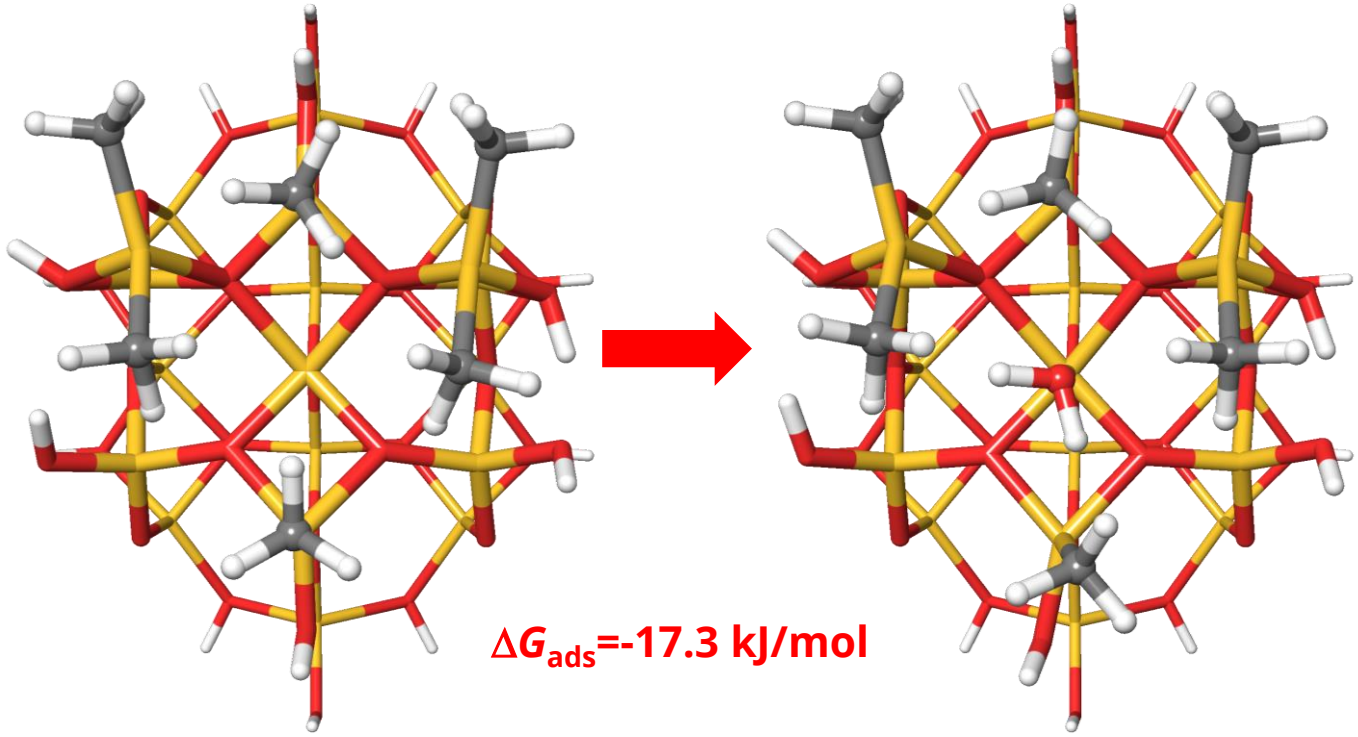
ΔG_{ads}=-31.4 kJ/mol

DFT-computed Gibbs free energies at 200°C and 1 atm, $T\Delta S(H_2O)$=89.4 kJ/mol

Adsorption of H_2O onto methylated surface



95.8 kJ/mol less stable isomer

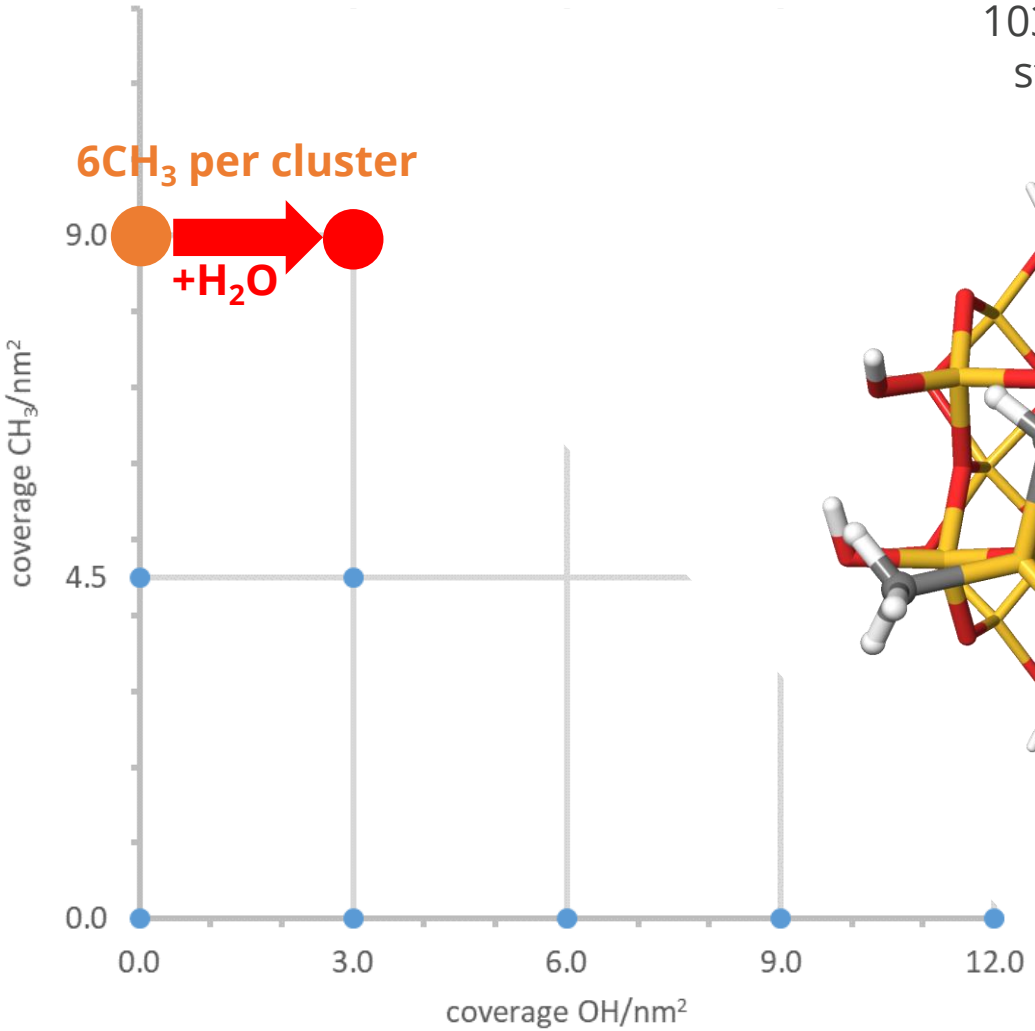


ΔG_{ads}=-17.3 kJ/mol

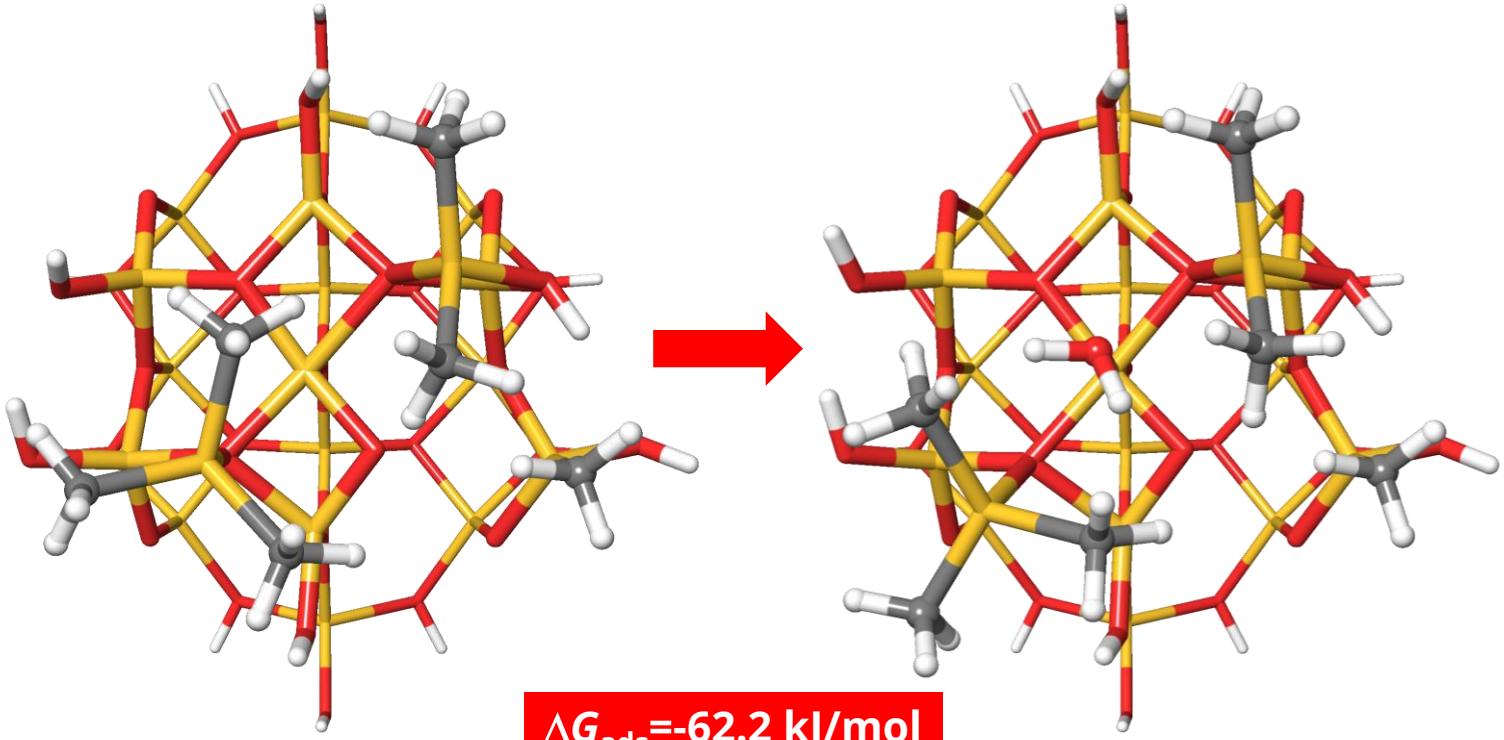
average over 5 methylated surfaces is ΔG_{ads}=-30±20 kJ/mol

DFT-computed Gibbs free energies at 200°C and 1 atm, $T\Delta S(H_2O)$=89.4 kJ/mol

Adsorption of H_2O onto methylated surface



103.9 kJ/mol less stable isomer

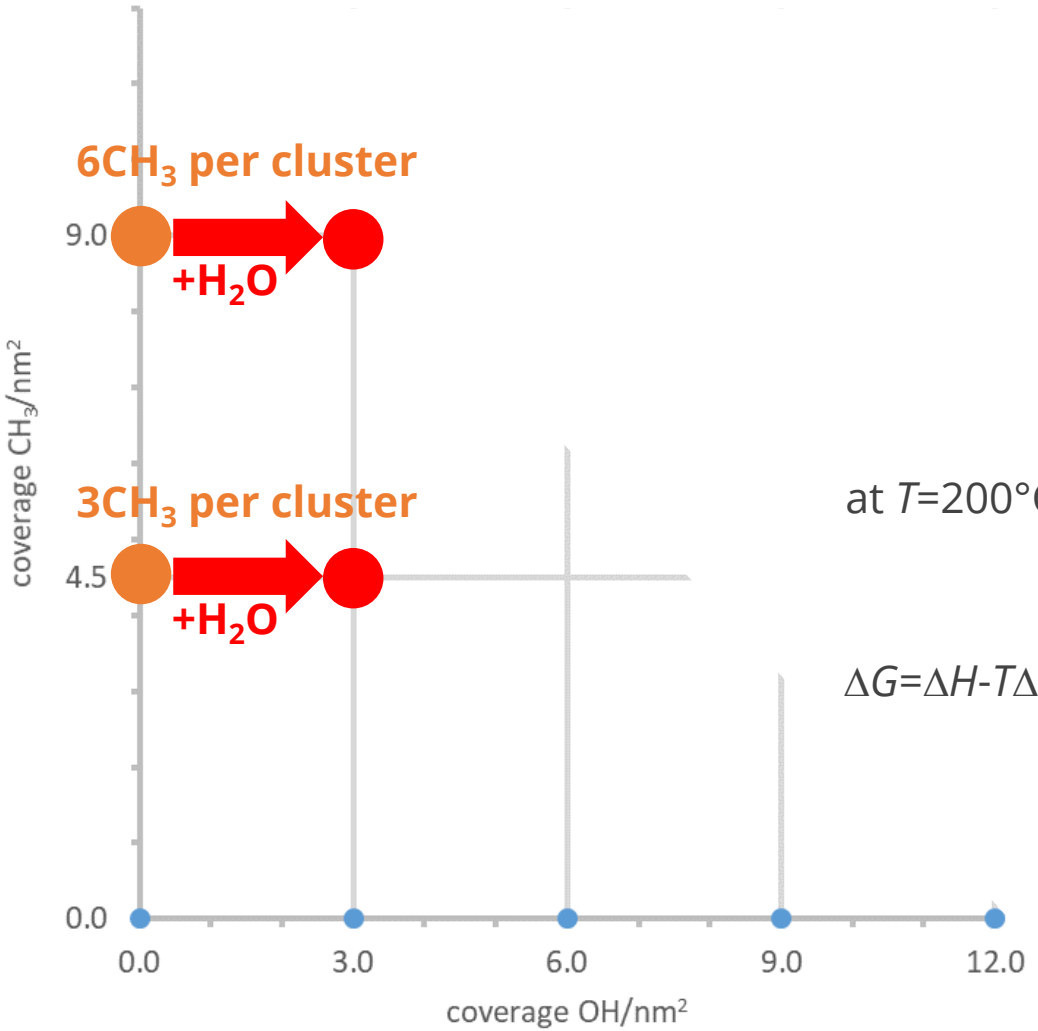


ΔG_{ads}=-62.2 kJ/mol

Contrary to what one would expect from sterics alone.

DFT-computed Gibbs free energies at 200°C and 1 atm, $T\Delta S(H_2O)$=89.4 kJ/mol

Adsorption of H_2O onto methylated surface



at T=200°C

$\Delta G=\Delta H-T\Delta S$

Predominant thermal effect is entropy of free H_2O molecule.

average ΔH_{ads}=-106±14 kJ/mol

constant $T\Delta S_{H2O}$=-89.4 kJ/mol

average $T\Delta S_{surf}$=+14±6 kJ/mol

average ΔG_{ads}=-30±20 kJ/mol

ΔH_{ads}=-128.7 kJ/mol

$T\Delta S_{H2O}$=-89.4 kJ/mol

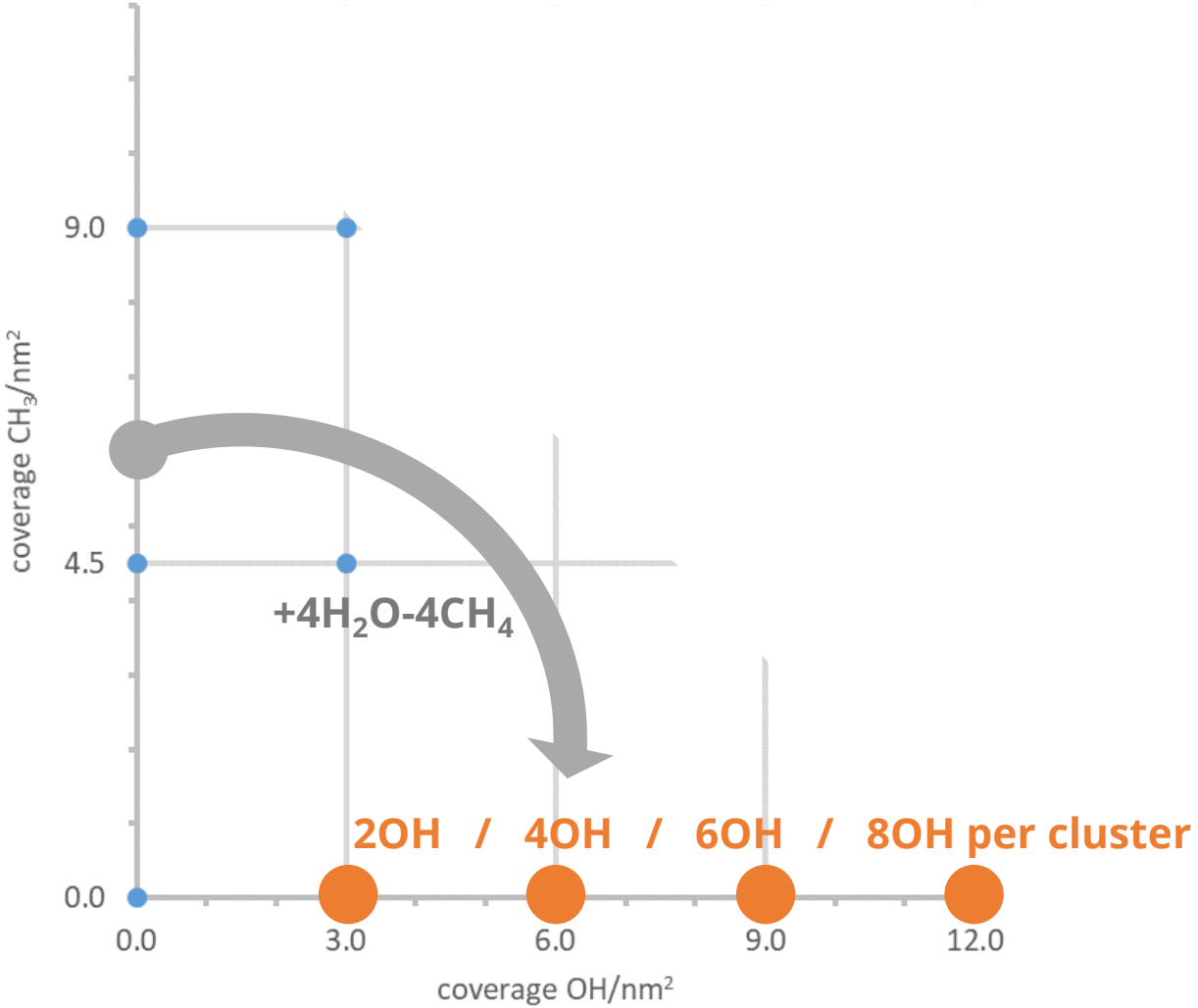
$T\Delta S_{surf}$=+22.8 kJ/mol

ΔG_{ads}=-62.2 kJ/mol

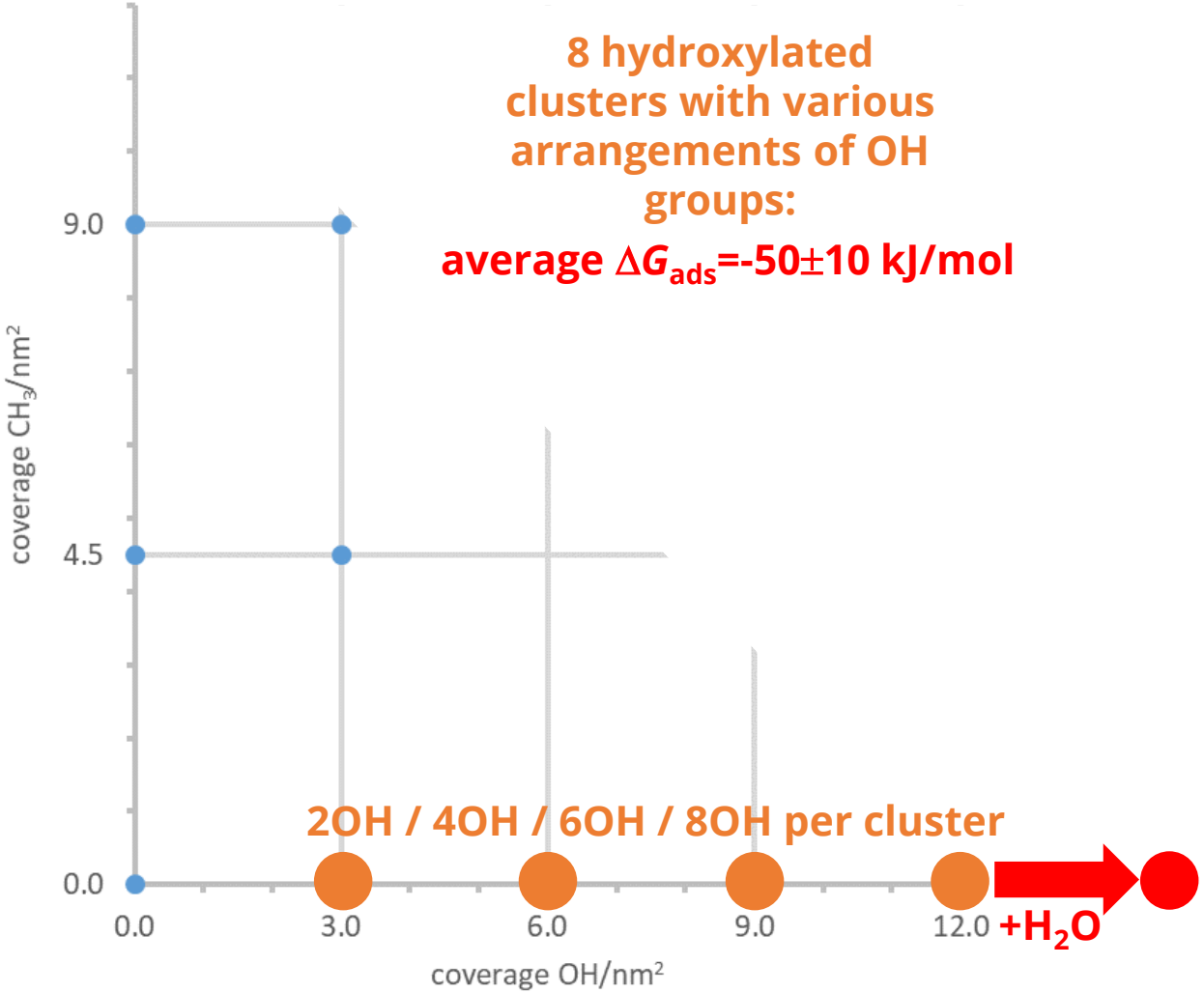
Entropy (=surface motion) plays a role here, but less than enthalpy (=bonding).

DFT-computed Gibbs free energies at 200°C and 1 atm, $T\Delta S(H_2O)$=89.4 kJ/mol

Adsorption of H_2O onto hydroxylated surface

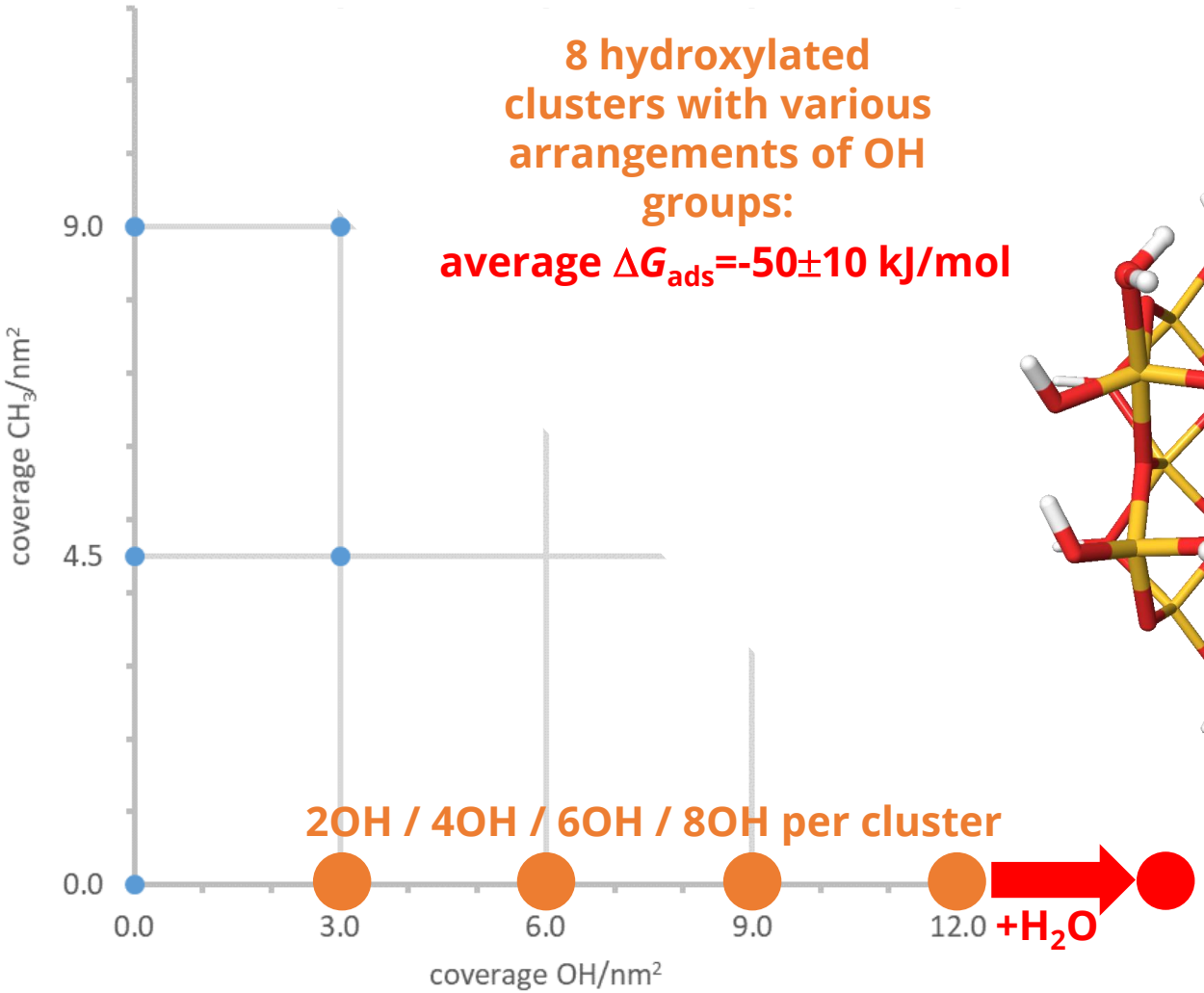


Adsorption of H_2O onto hydroxylated surface



DFT-computed Gibbs free energies at 200°C and 1 atm, $T\Delta S(H_2O)$=89.4 kJ/mol

Adsorption of H_2O onto hydroxylated surface



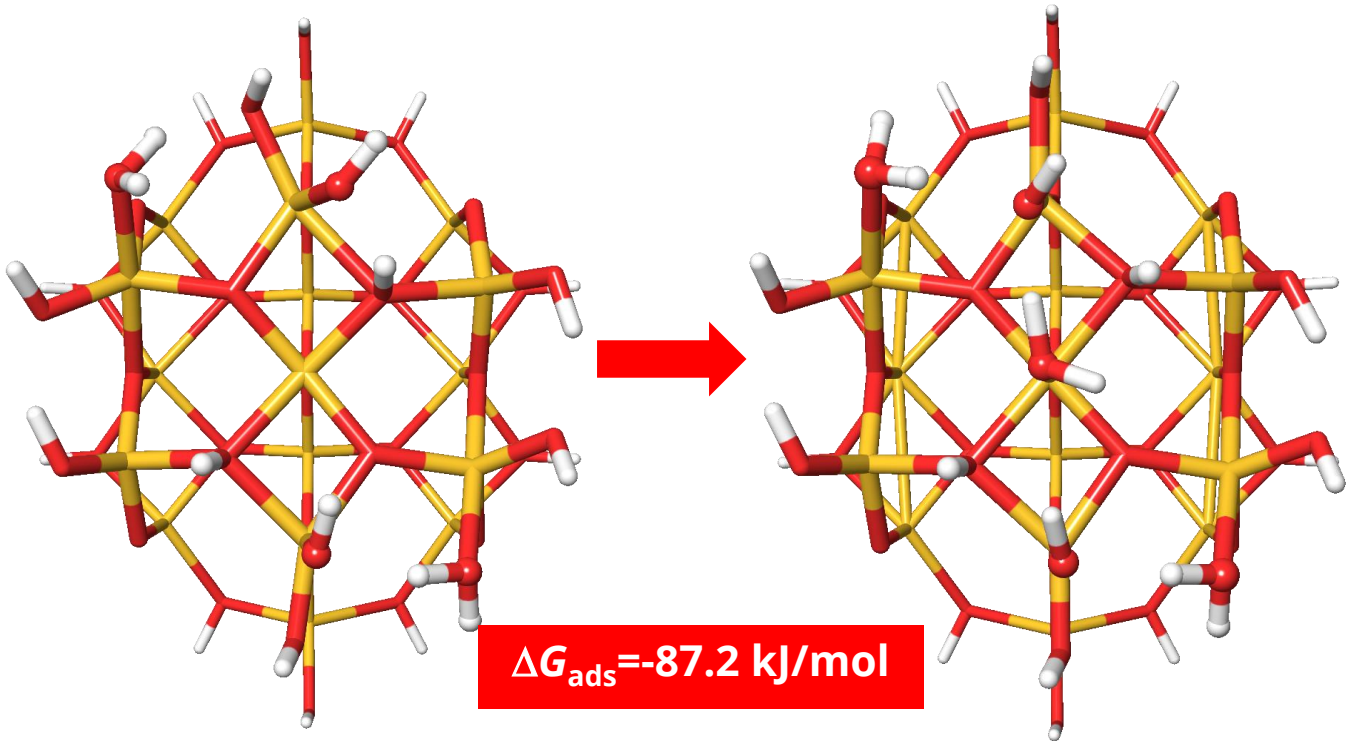
8 hydroxylated clusters with various arrangements of OH groups:

average ΔG_{ads}=-50±10 kJ/mol

2OH / 4OH / 6OH / 8OH per cluster

+H_2O

8OH per cluster



ΔG_{ads}=-87.2 kJ/mol

DFT-computed Gibbs free energies at 200°C and 1 atm, $T\Delta S(H_2O)$=89.4 kJ/mol

Next step:
enumeration of reactions of adsorbed H_2O

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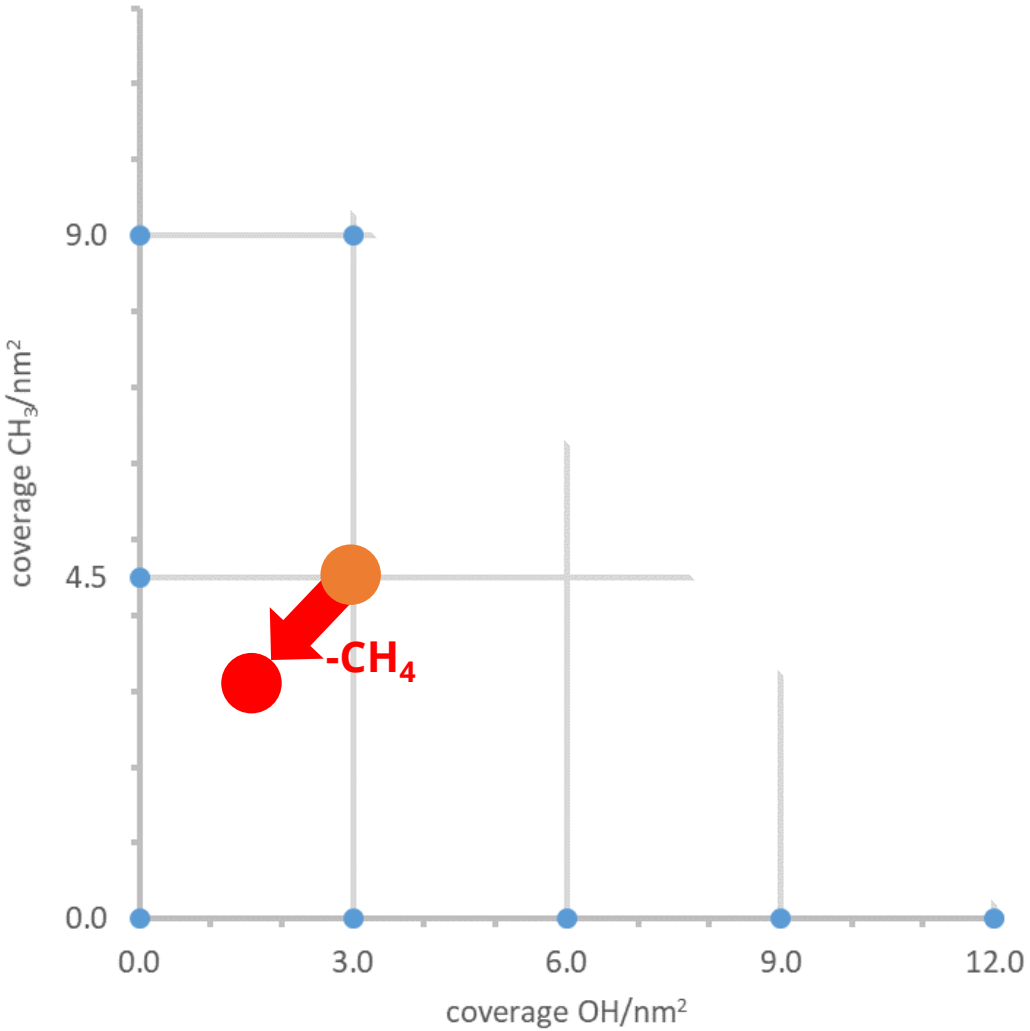
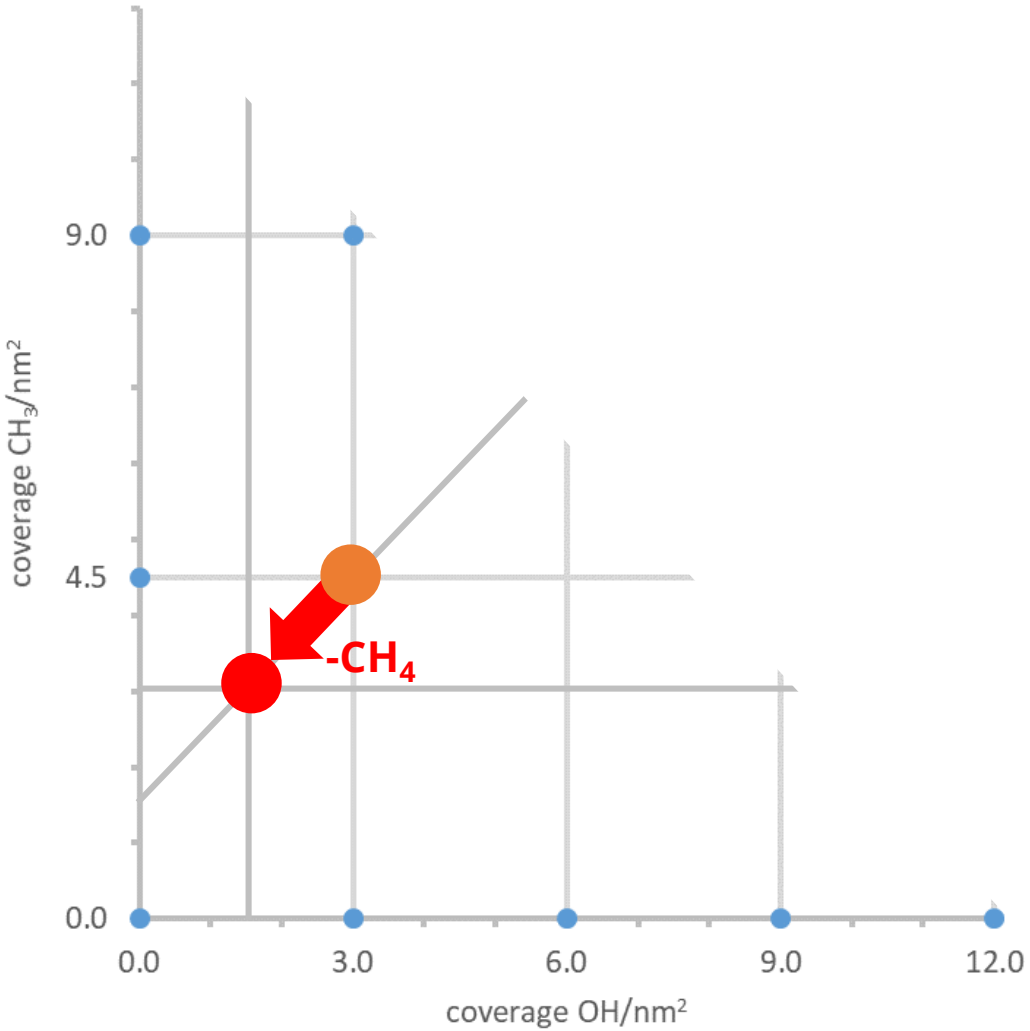
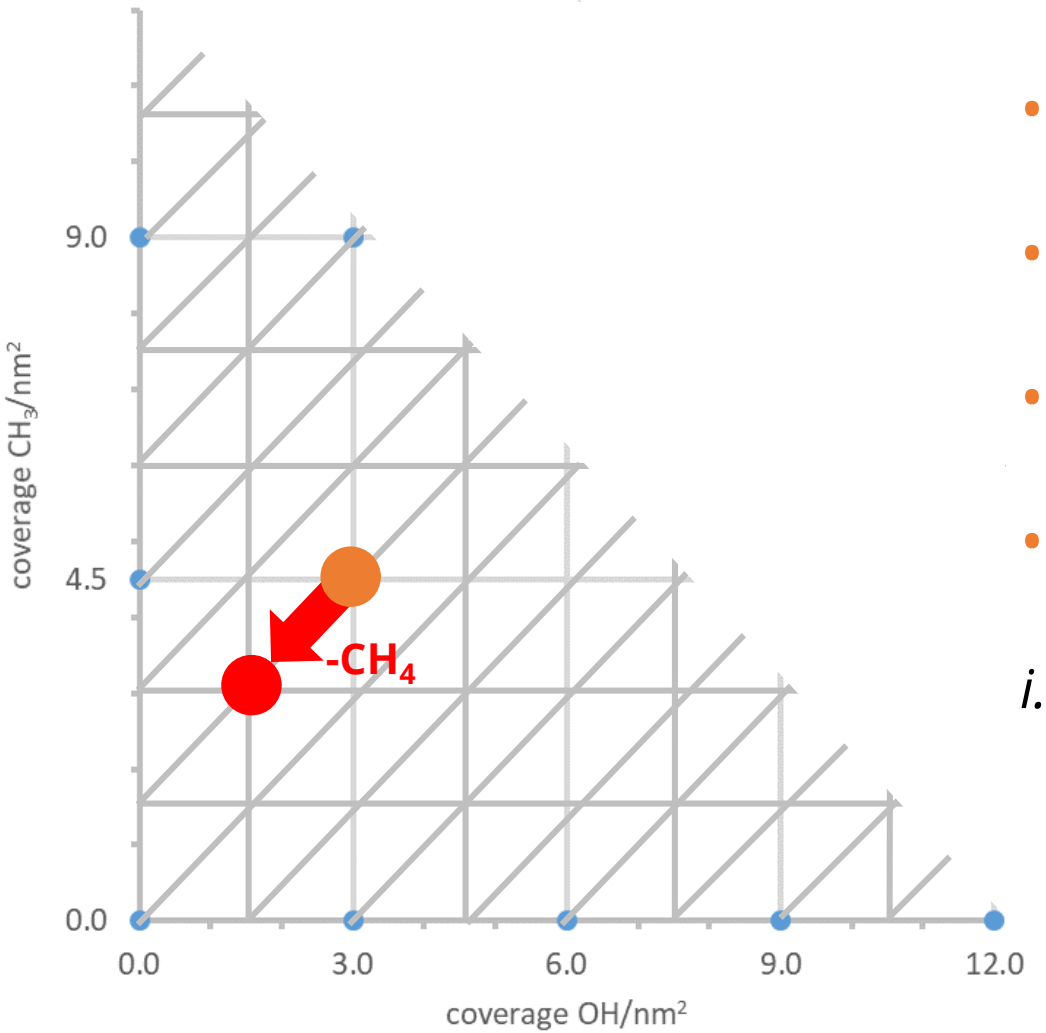
CH_3/H-transfer and elimination of CH_4



CH_3/H-transfer and elimination of CH_4



CH_3/H-transfer and elimination of CH_4



- About 5x more concentrations to consider in chemical space.
- Enumeration of isomers at each concentration, as before.
- Multiple reaction paths for H-transfer are possible for each isomer.
- Finding transition states takes more cpu time and is less reliable than finding minima.

i.e. **MUCH MORE DEMANDING CALCULATIONS**

Conclusions about automated enumeration

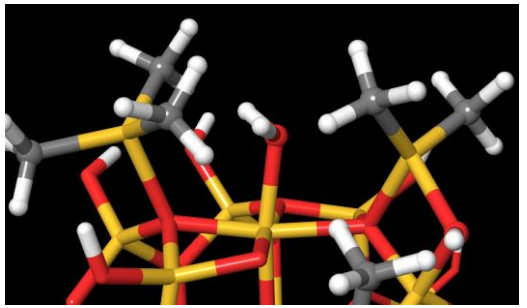
Chemical space is big!

- Systematic enumeration over structural isomers is achievable.
  - However, not entirely automatic: must check for exotic/outlier chemistries, as they may skew results.
- Enumeration over all possible reaction pathways between isomers is currently a challenge.
- CPU time required for quantum mechanical calculations remains a significant limiting factor.

Conclusions about cooperative effect

- Molecular adsorption of H_2O onto a 5-coordinate surface Al site is computed to be barrierless in nearly all cases studied.
- Little evidence of cooperative effect on thermodynamics:
  - Onto methylated surface, average ΔG_{ads}=-30±20 kJ/mol at 200°C.
  - Onto hydroxylated surface, average ΔG_{ads}=-50±10 kJ/mol at 200°C.

  except for some individual cases outside these ranges, which merit more detailed study.
- Contribution from 3D-flexibility of the surface (in terms of both enthalpy and entropy) can be effectively treated with cluster model.



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