Selective Deposition of Pd onto Silica Supported Iron for Maintaining Fe^0 during Hydrodeoxygenation

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SECS

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Outline

- Motive and Background
- Target and Challenges
- Potential Solution: Pd-Fe
- Strong Electrostatic Adsorption (SEA)
- SEA on silica-supported Fe_2O_3
- Synthesis and Characterization
  - Uptake Surveys
  - Temperature Programmed Reduction
  - In-Situ XRD reduction
- Conclusions

Biomass to drop-in fuel: step 1

Cellulose
Hemicellulose
Lignin

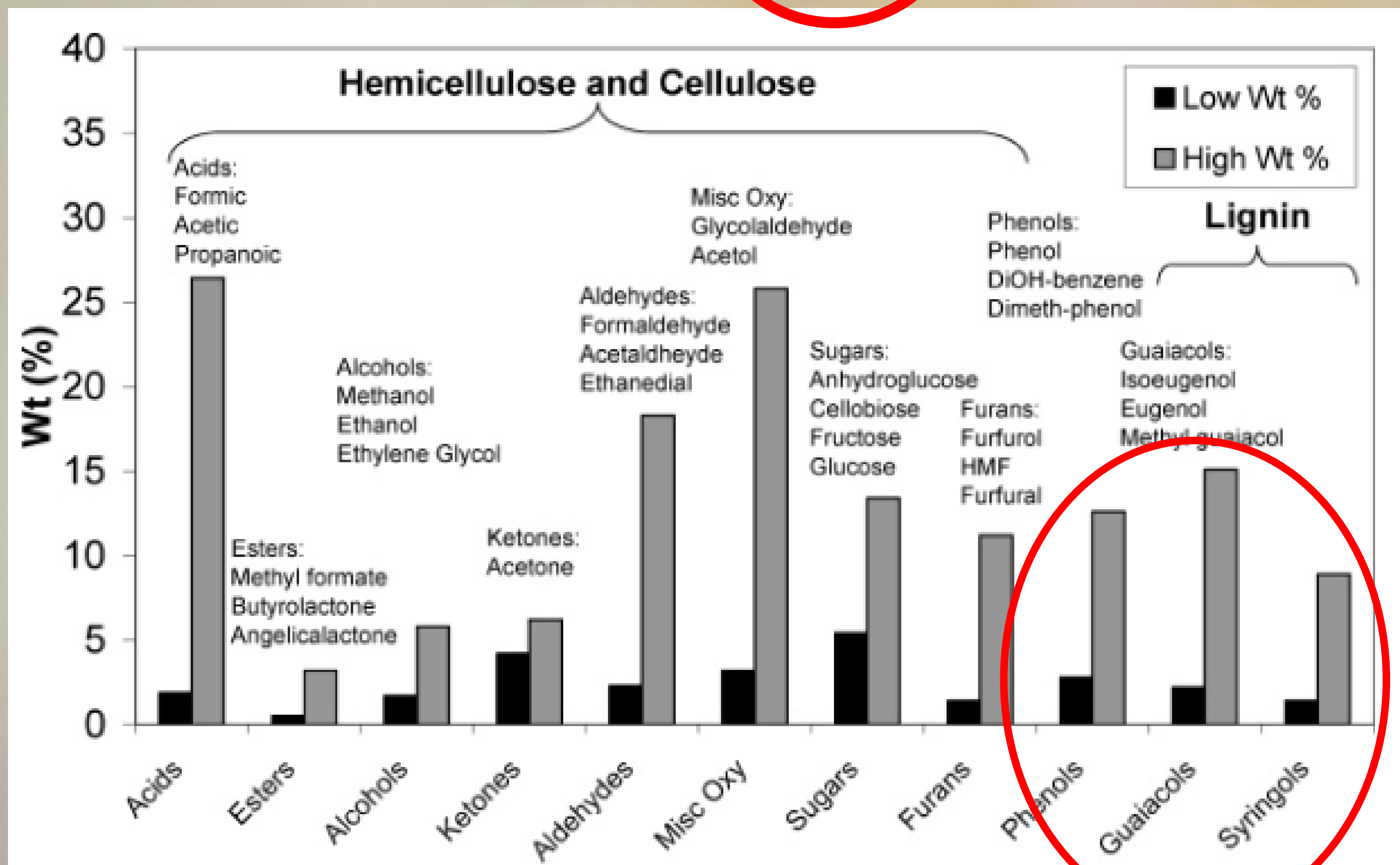
Pyrolysis

Photo by Dennis Schroeder, NREL 20404. Reliable Characterization for Pyrolysis Bio-Oils Leads to Enhanced Upgrading Methods. https://www.nrel.gov/research/highlights/reliable-characterization-pyrolysis.html.

Biomass to drop-in fuel: step 2

Remove oxygen from bio-oil

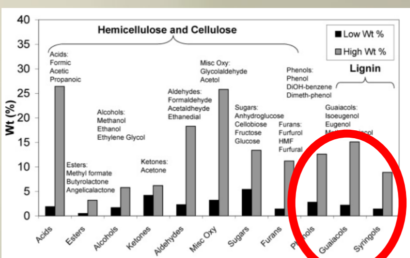
Photo by Dennis Schroeder, NREL 20404.

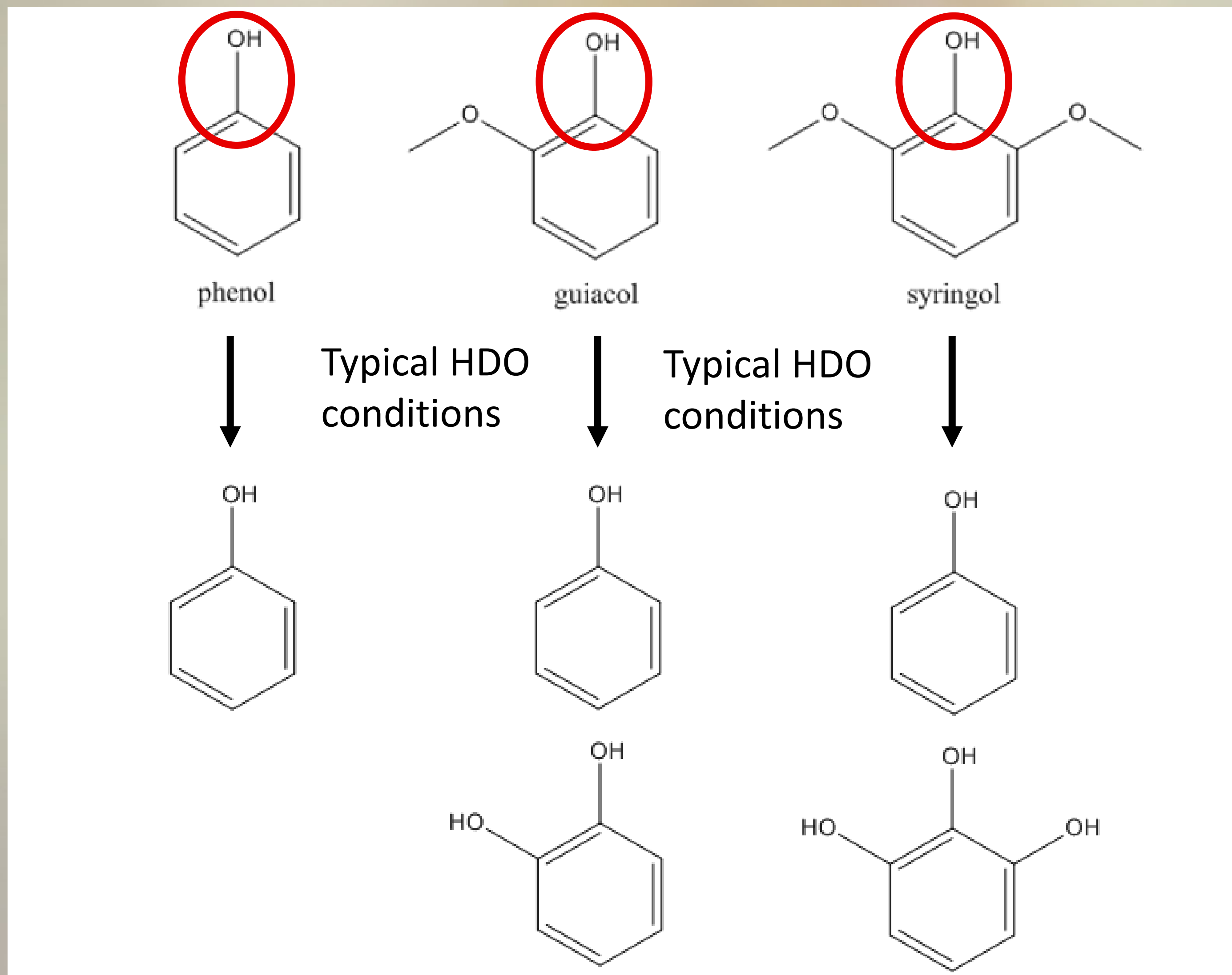


Chemical composition of bio-oil [1], as summarized in [2]

Target

Toughest Deoxygenation: the phenolic C-O bond

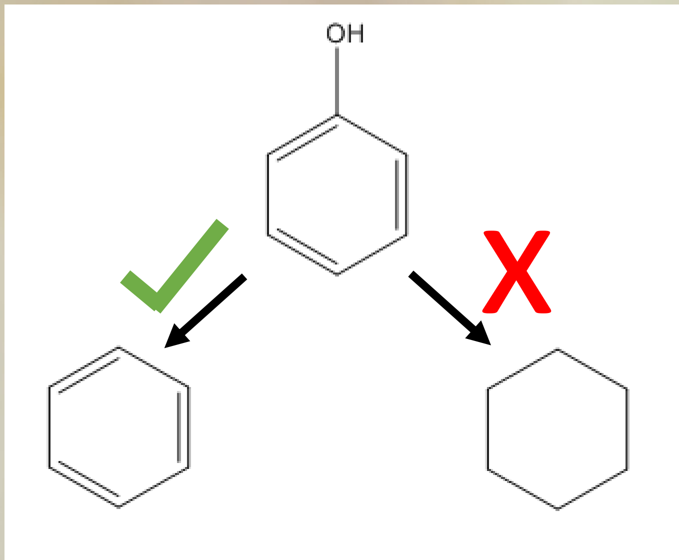




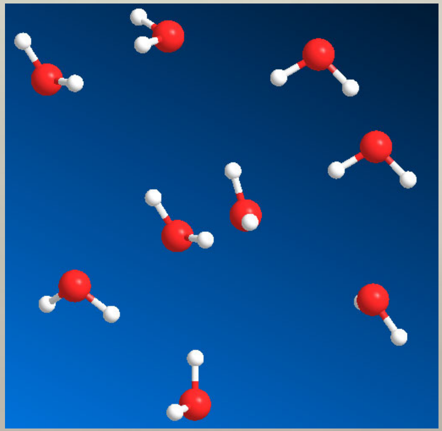
Challenges

Additional difficulties:

- Selectively breaking C-O bond
  - Uses less hydrogen
  - Preserving aromaticity keeps octane value high



- Water in bio-oil: deactivates catalysts by oxidation



Potential Solution: Pd-Fe

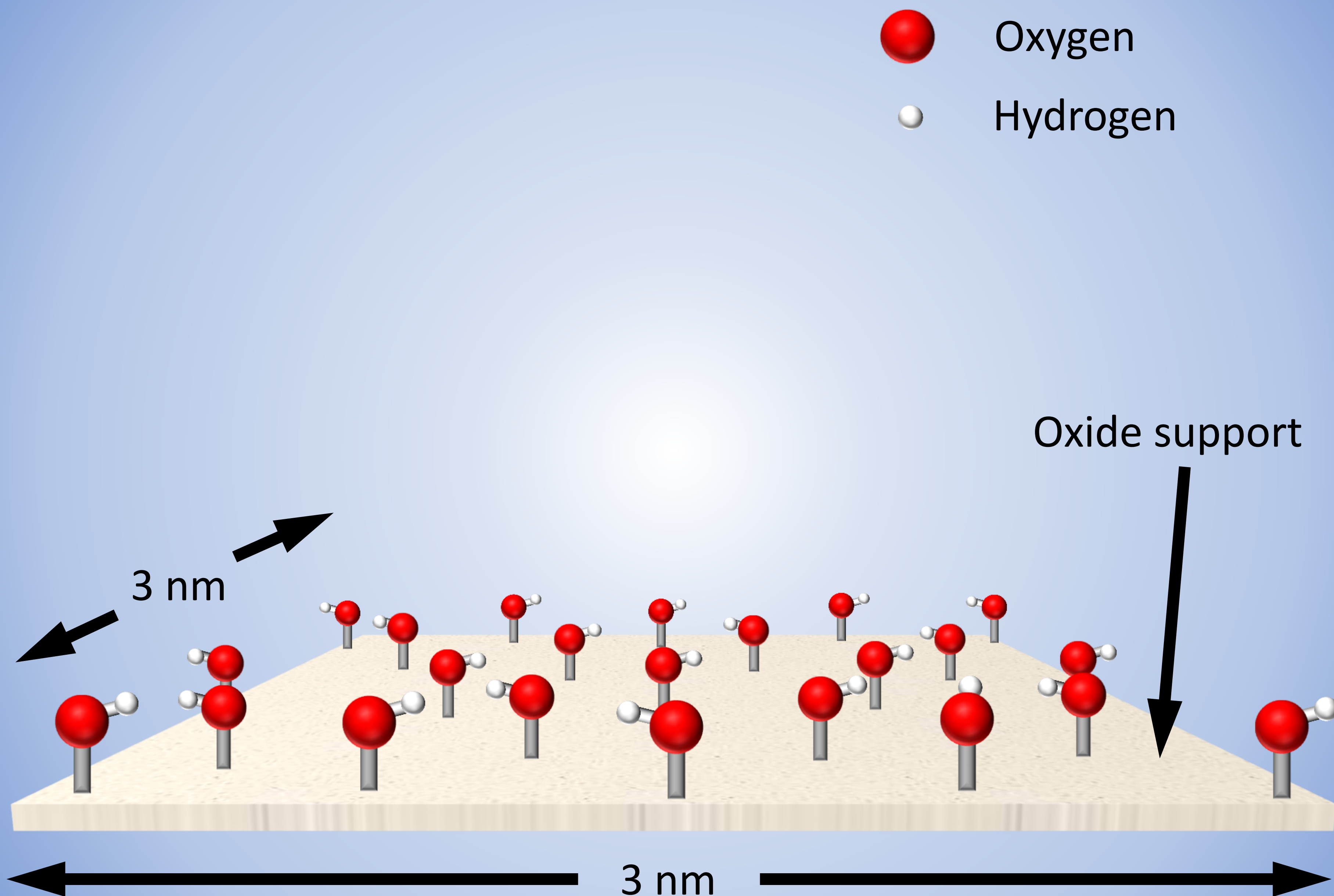
Why Pd-Fe? For gas phase HDO:

- Fe^0 has high selectivity, but low activity and quick deactivation by water[3,4]
- Pd has low selectivity, but high activity and stability[5]
- Synergistic effect gives high selectivity and activity[6,7,8]
- Pd also stabilizes Fe against deactivation[9,10]

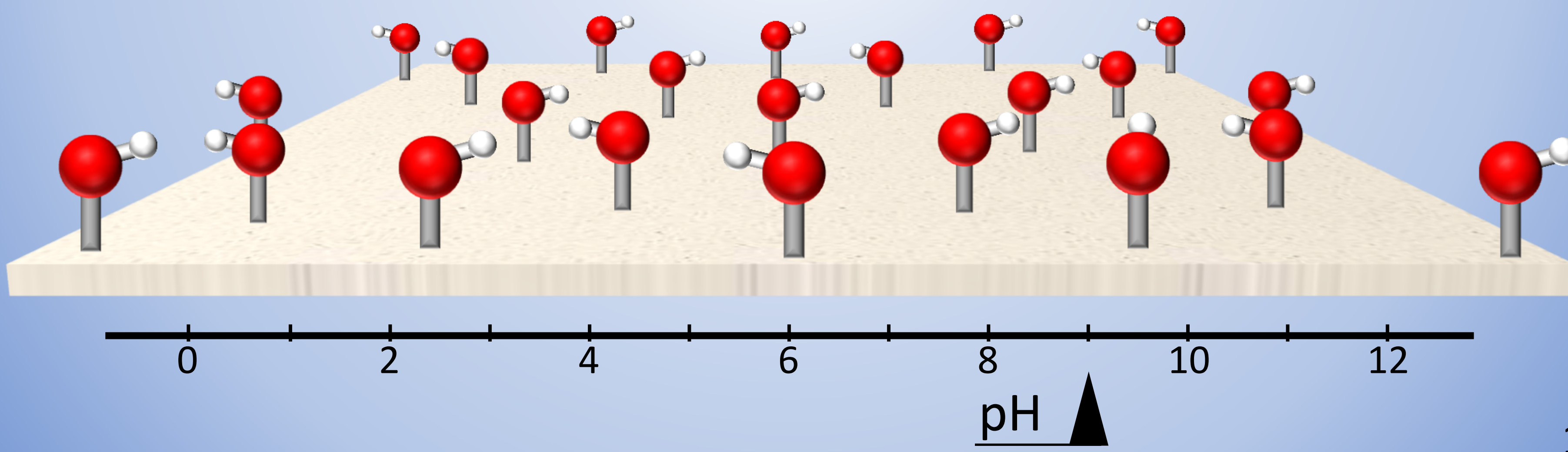
Hypothesis

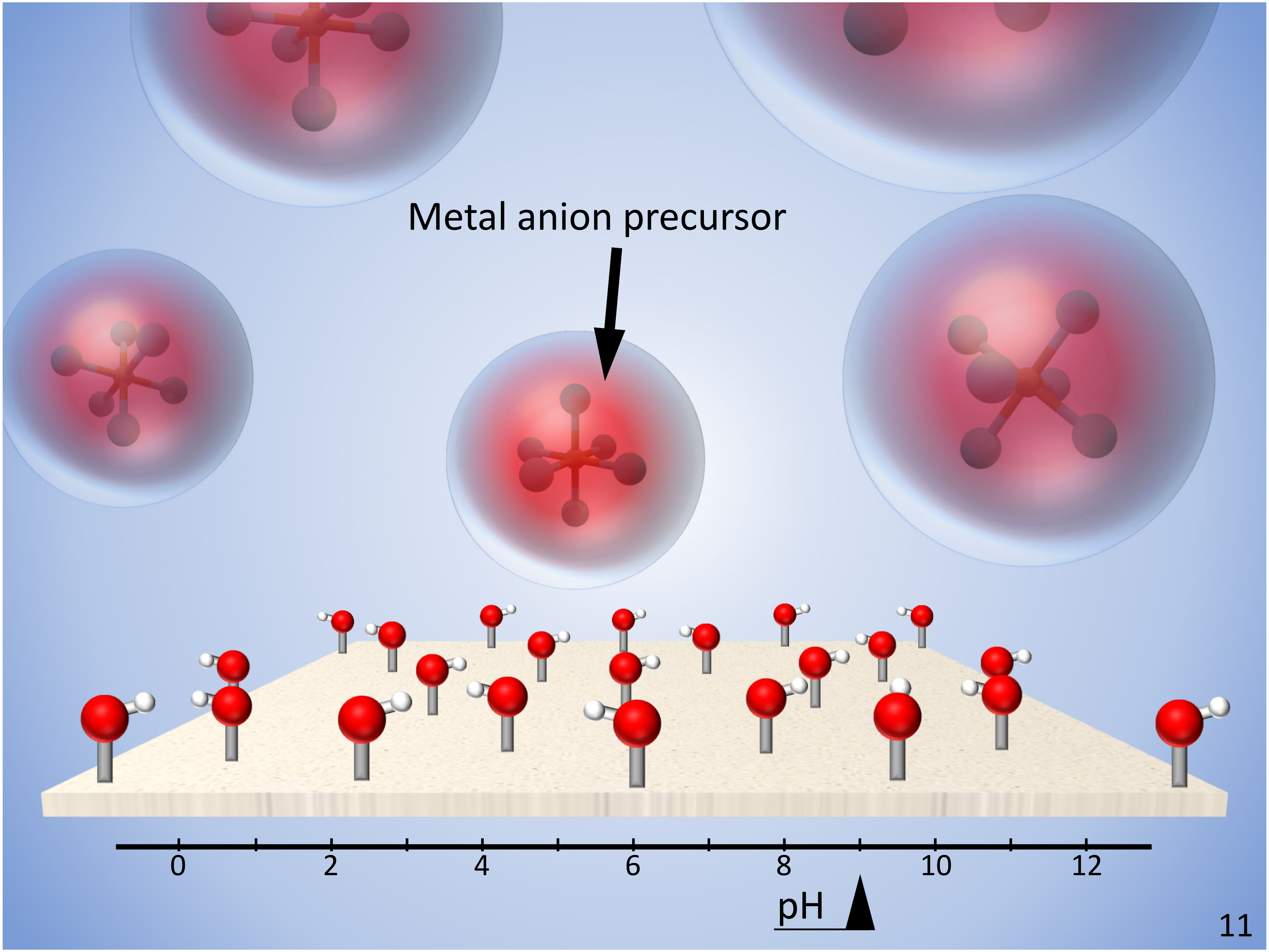
Pd-Fe catalysts with a higher Fe utilization and better stability against water oxidation (via a more thorough Pd-Fe interaction) might be achieved by depositing Pd selectively onto supported iron oxide particles using SEA prior to reduction

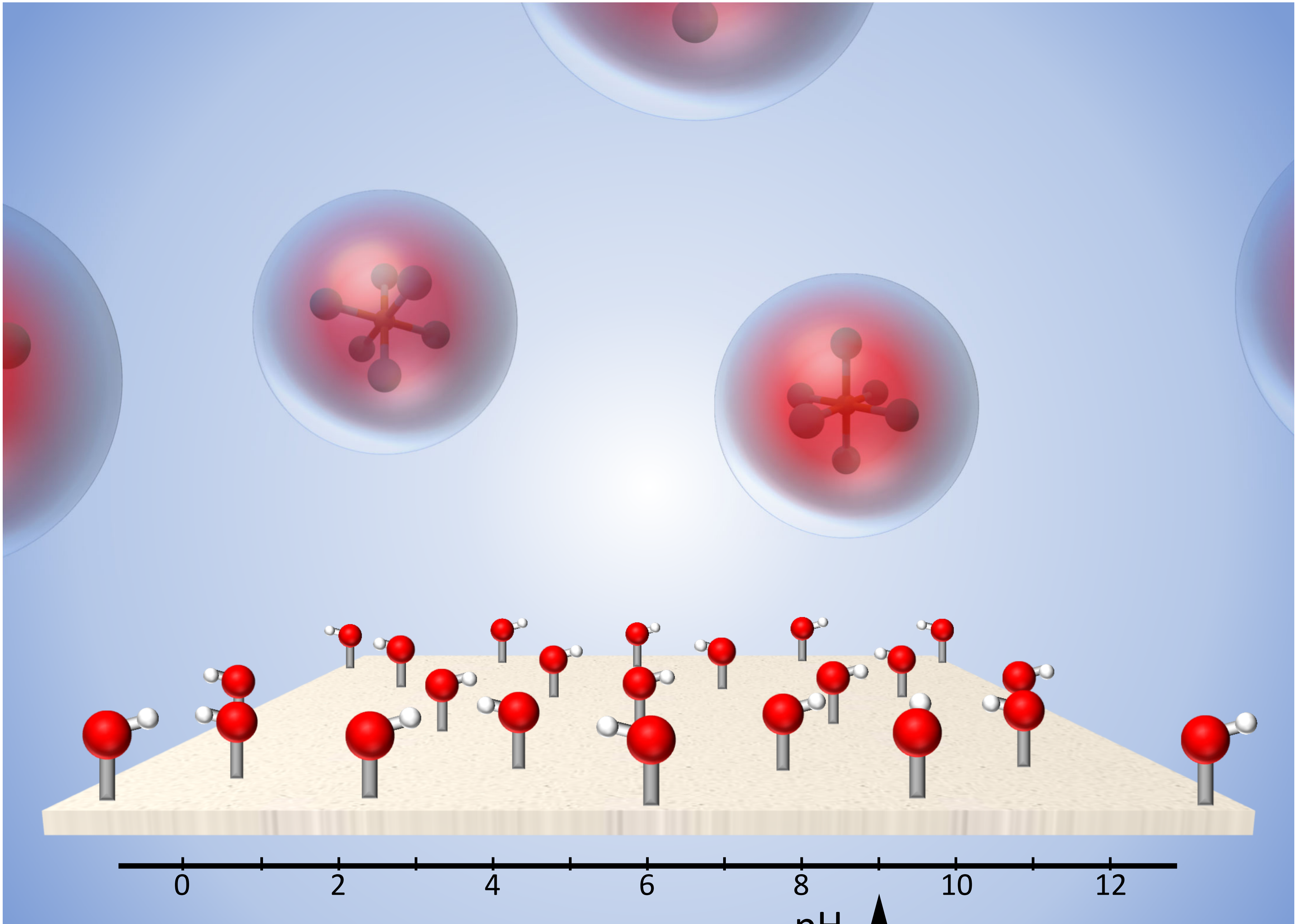
Strong Electrostatic Adsorption (SEA)

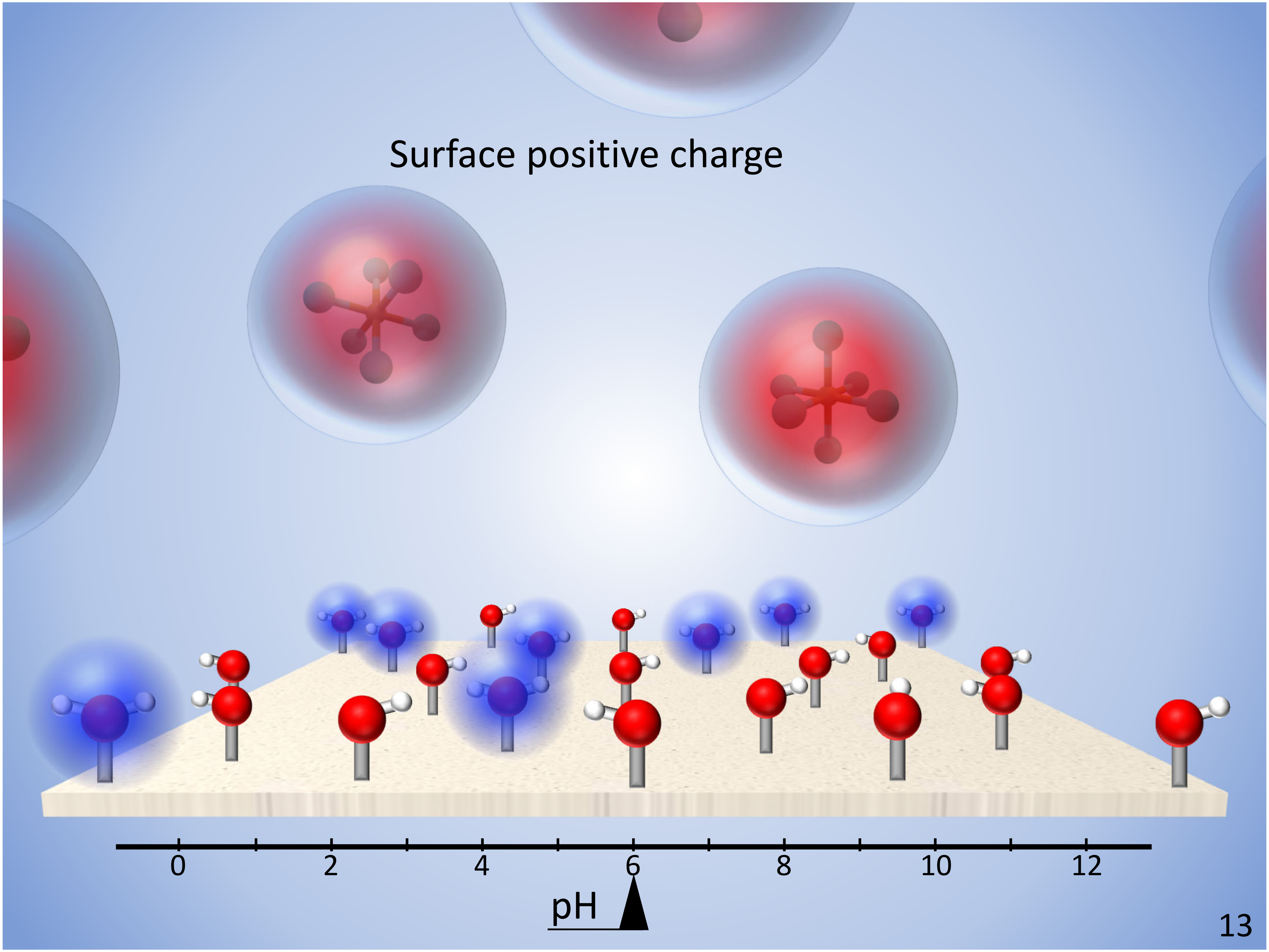

Oxygen
Hydrogen
Oxide support
3 nm
3 nm

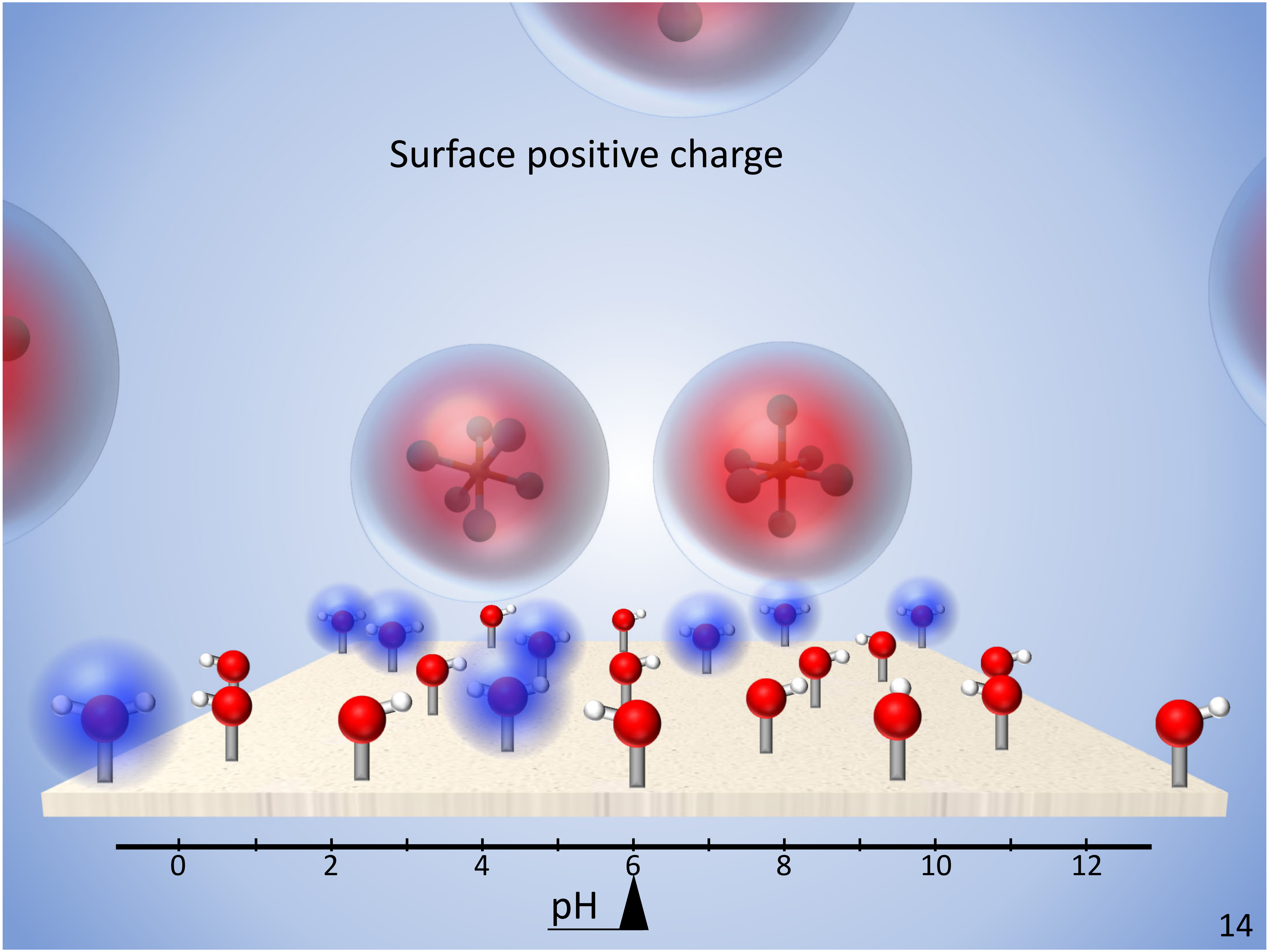
Point of Zero Charge (PZC)

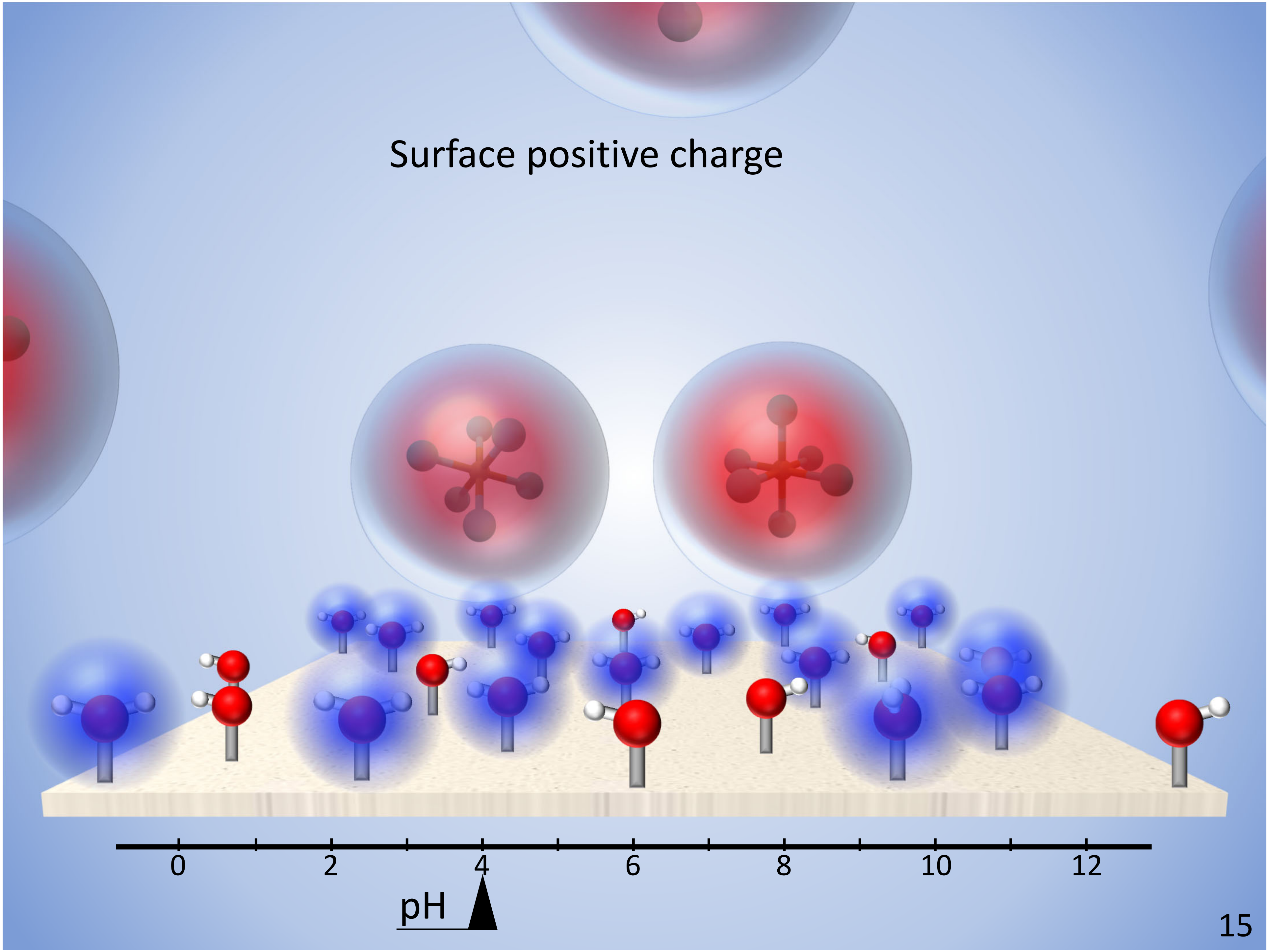



Metal anion precursor
0
2
4
6
8
10
12
pH

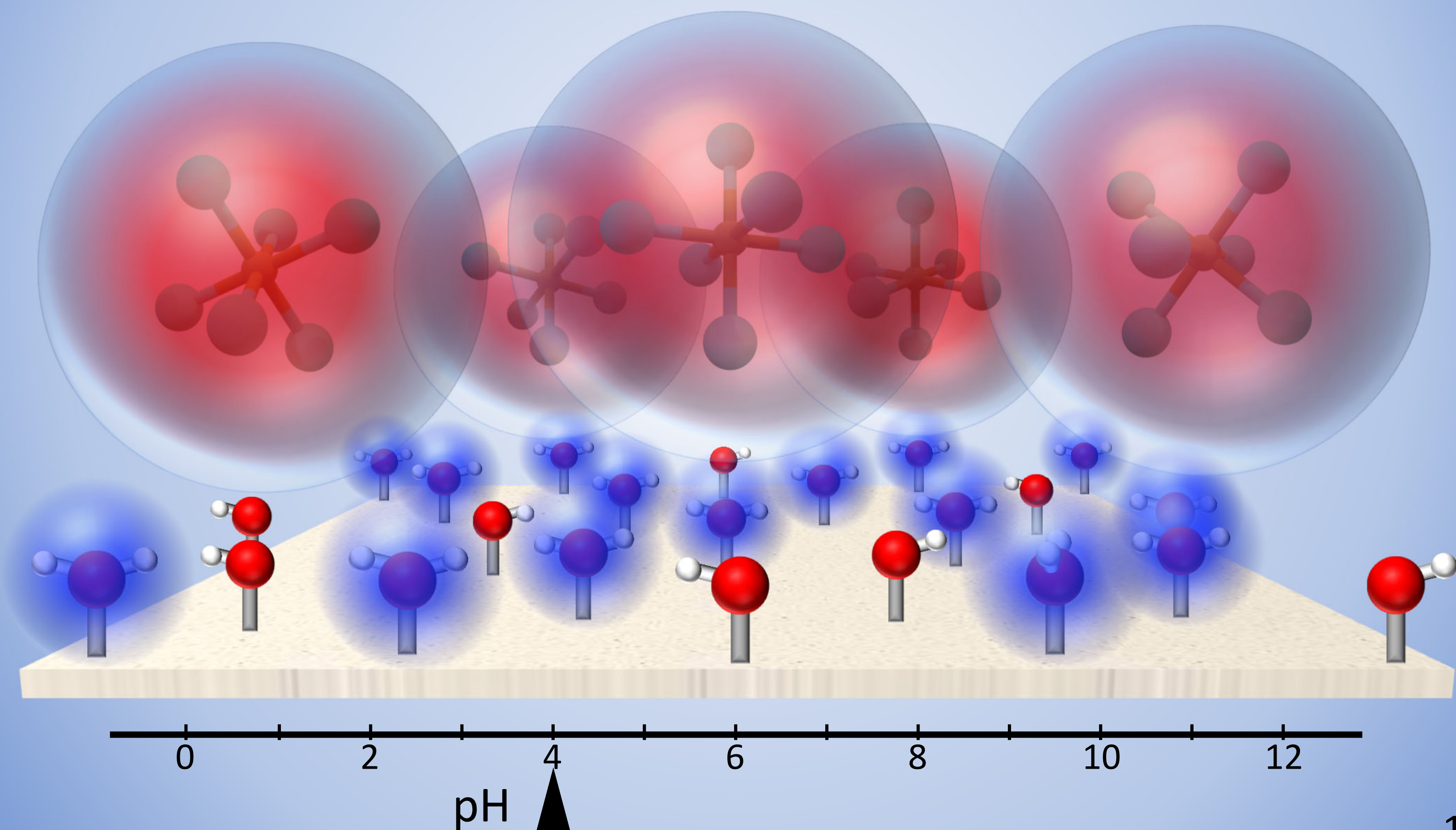

0
2
4
6
8
10
12
pH


Surface positive charge
0
2
4
6
8
10
12
pH

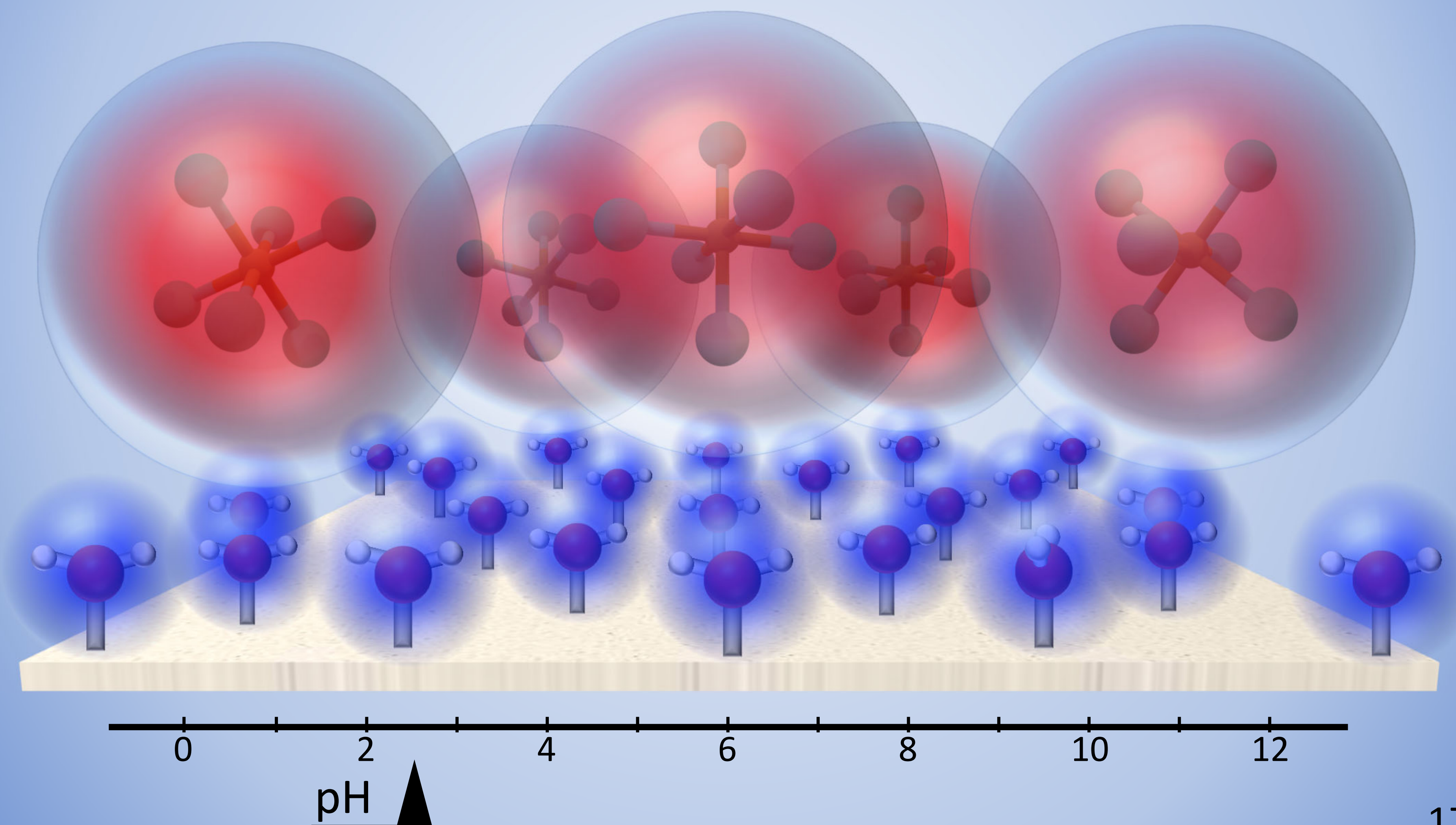

Surface positive charge
0
2
4
6
8
10
12
pH

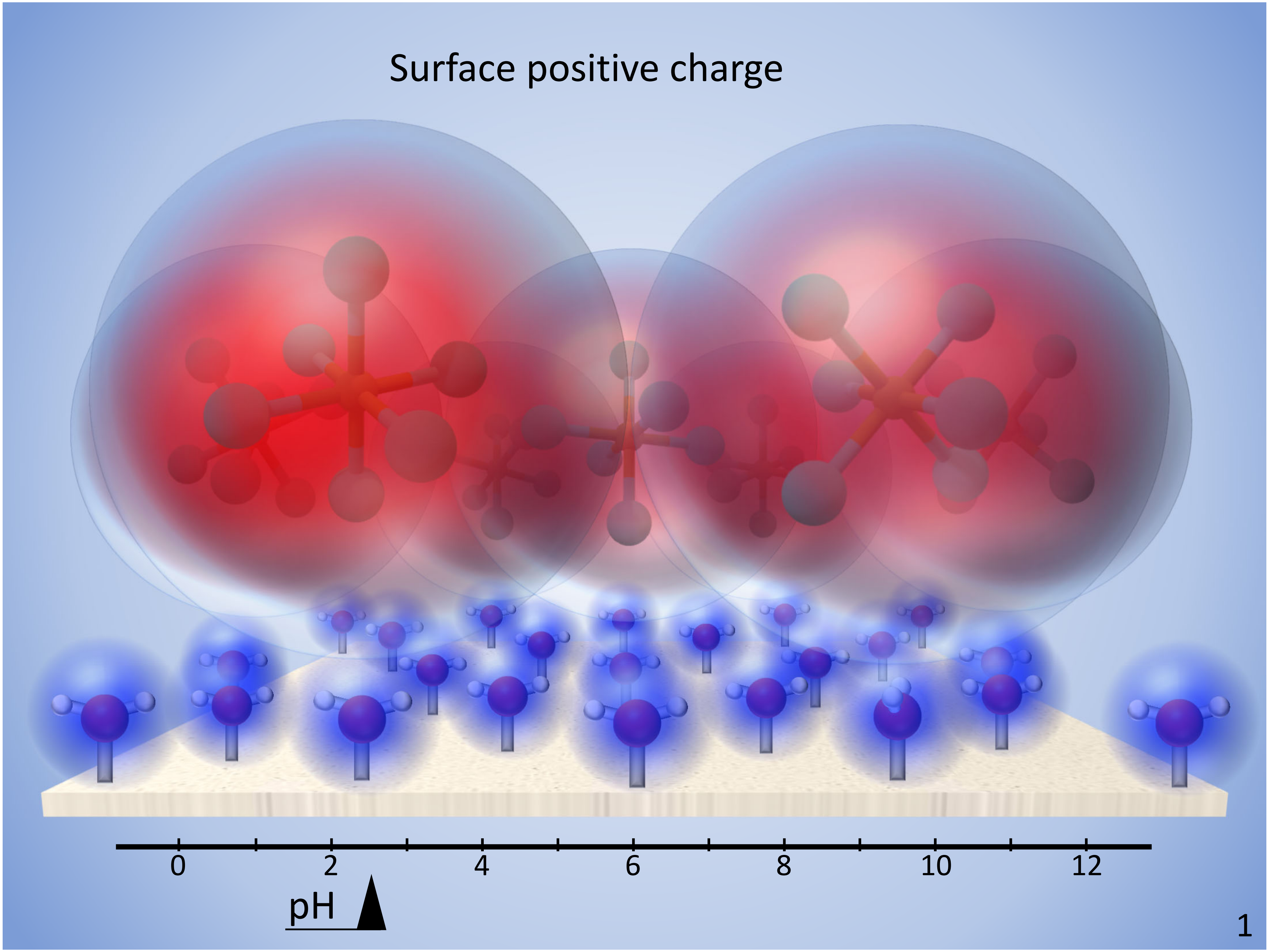

Surface positive charge
0
2
4
6
8
10
12
pH

Surface positive charge

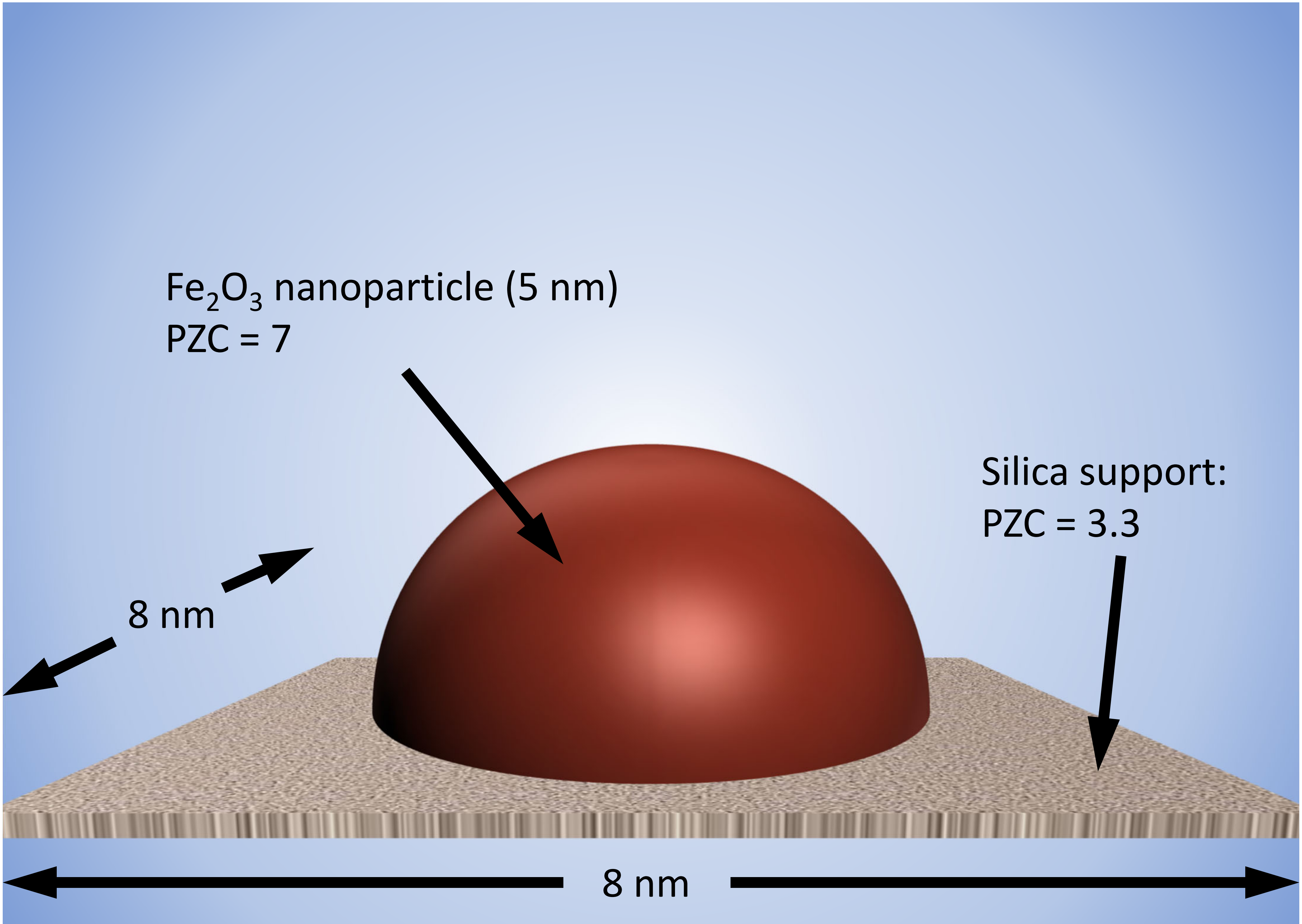


Surface positive charge

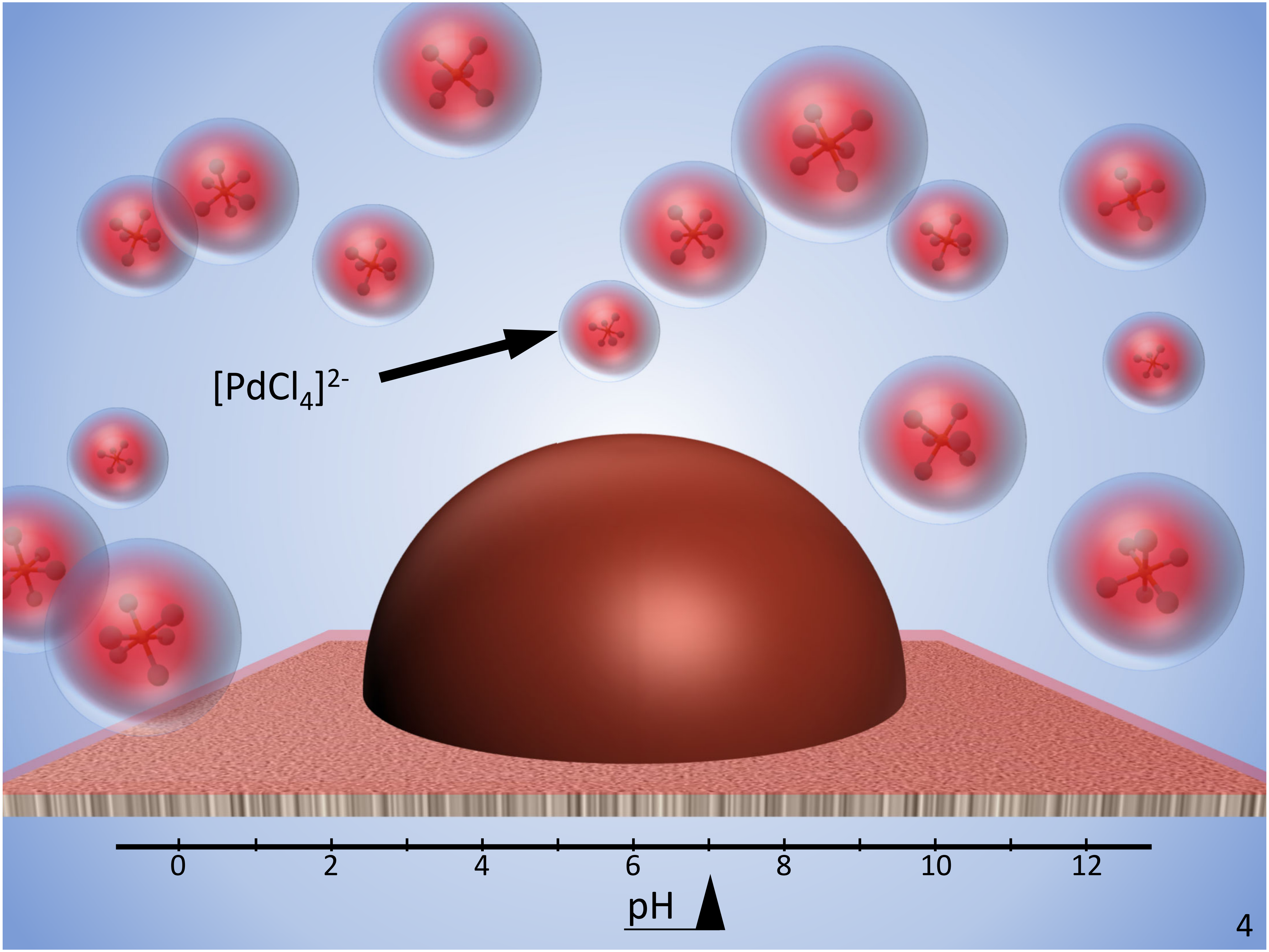



Surface positive charge
0
2
4
6
8
10
12
pH

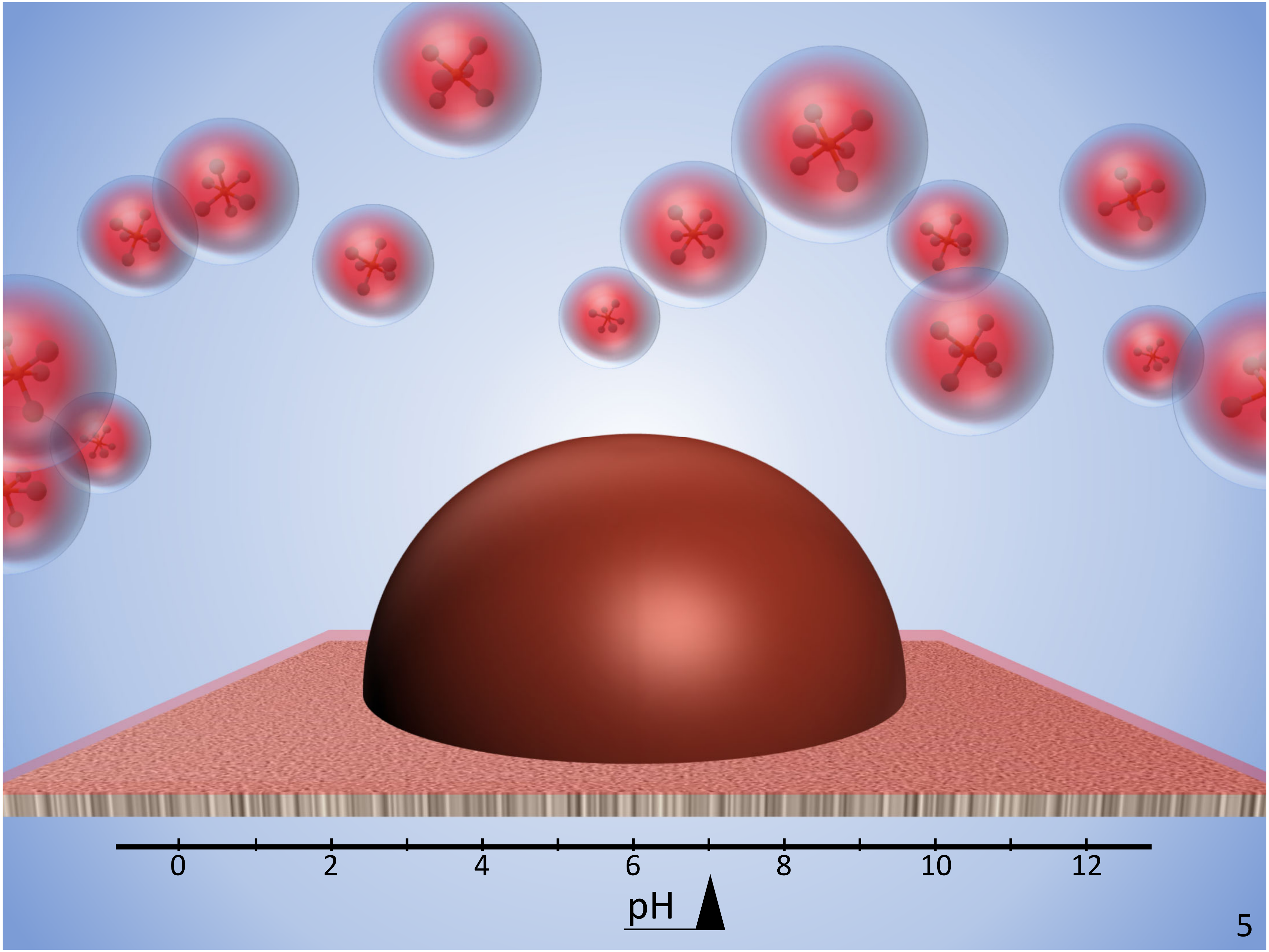
SEA on silica-supported Fe_2O_3



Fe_2O_3 nanoparticle (5 nm)
PZC = 7
Silica support:
PZC = 3.3
8 nm
8 nm



$[PdCl_4]^{2-}$
0
2
4
6
8
10
12
pH
4


0
2
4
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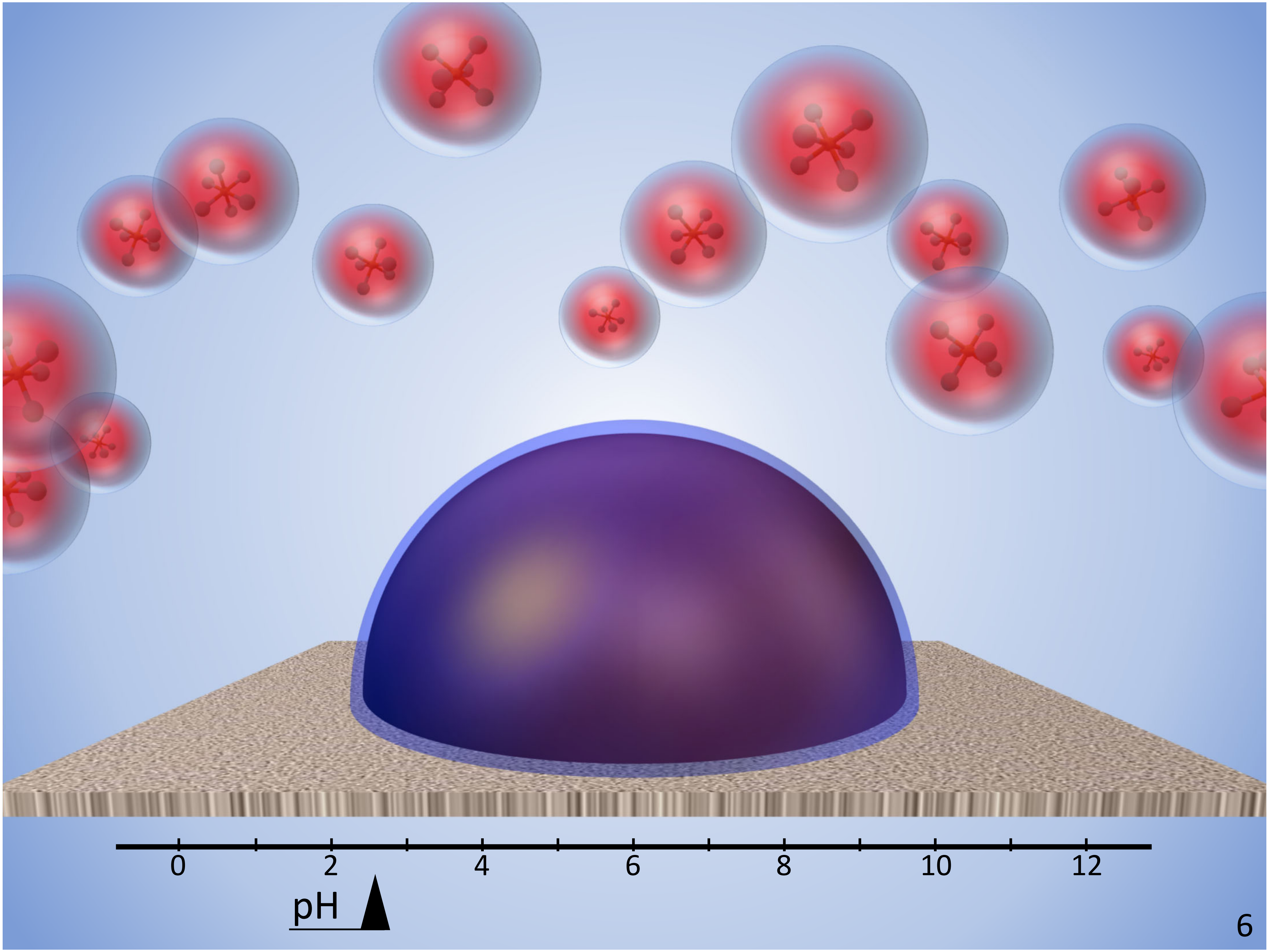
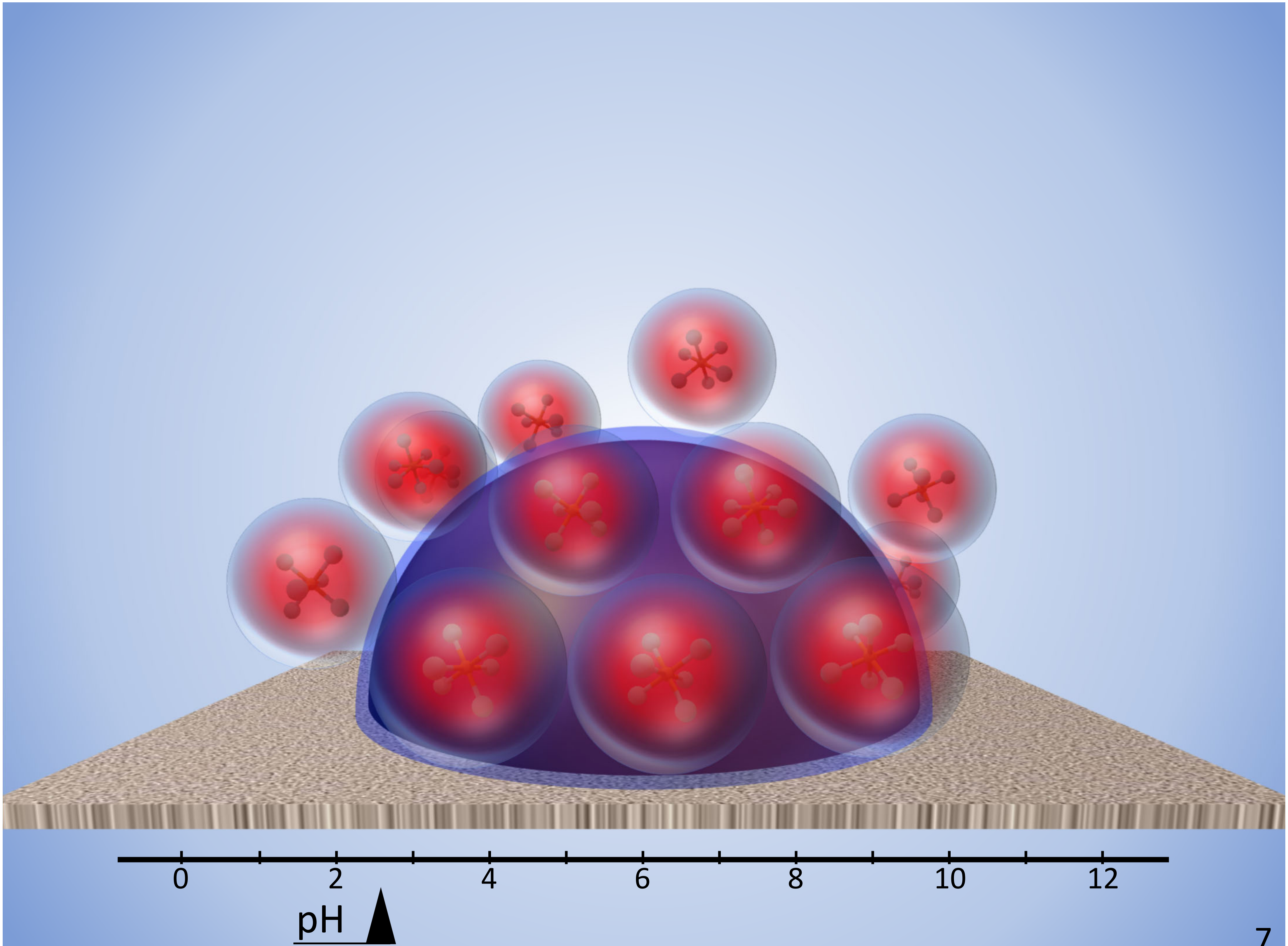
8
10
12
pH


0
2
4
6
8
10
12
pH
6

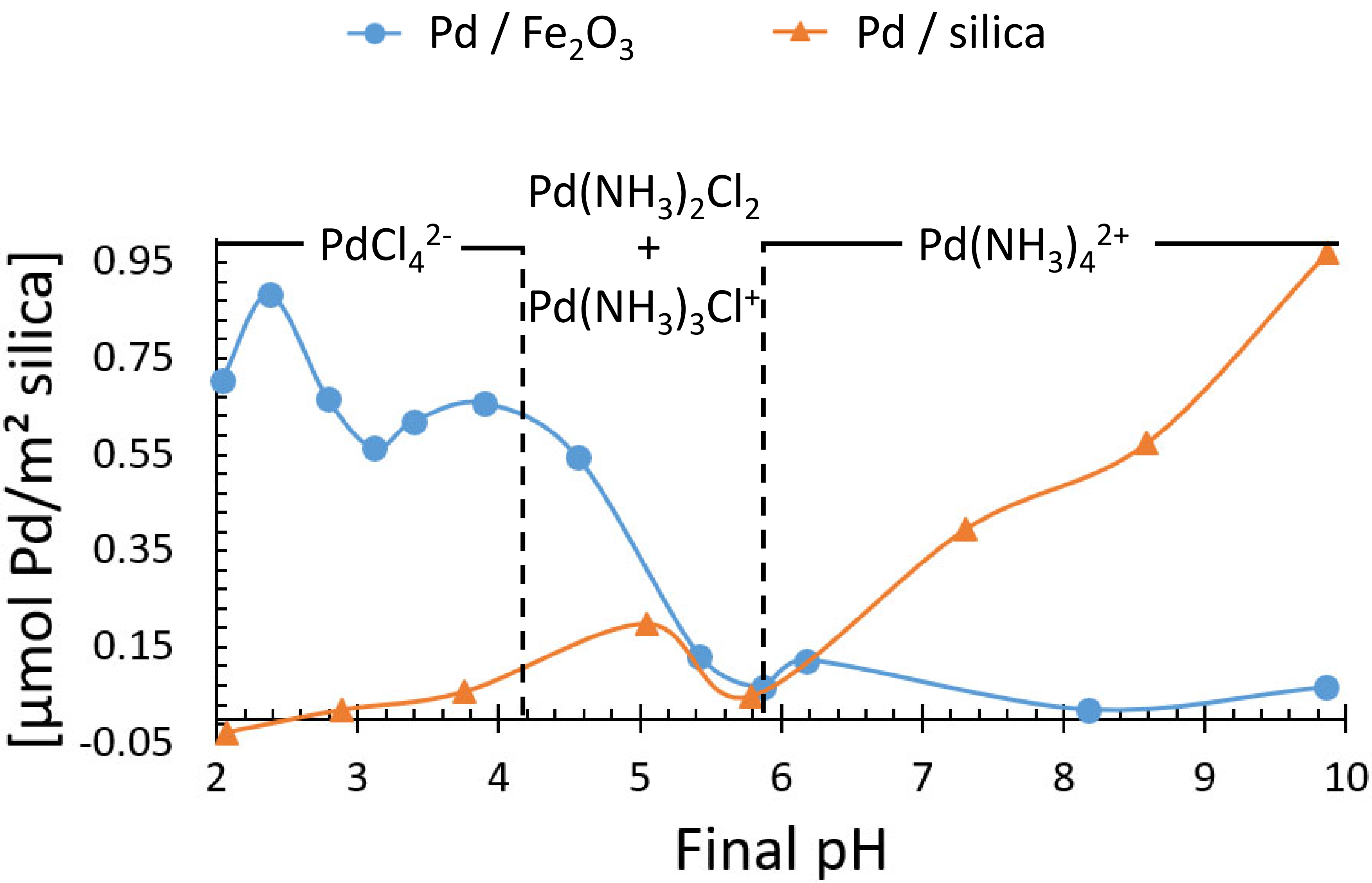

0
2
4
6
8
10
12
pH

Synthesis and Characterization

Synthesis and Characterization

Question	Technique used to answer
What pH values to use for SEA synthesis?	Uptake Survey using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)
What is the weight loading of the Pd?	ICP-OES
How much interaction between Pd and Fe?	Temperature Programmed Reduction (TPR)
What crystallite phases are present?	X-ray Diffraction
What are the crystallite sizes of each phase?	X-ray Diffraction

Uptake Survey results: Use pH 2.5



*Pd speciation from reference 11

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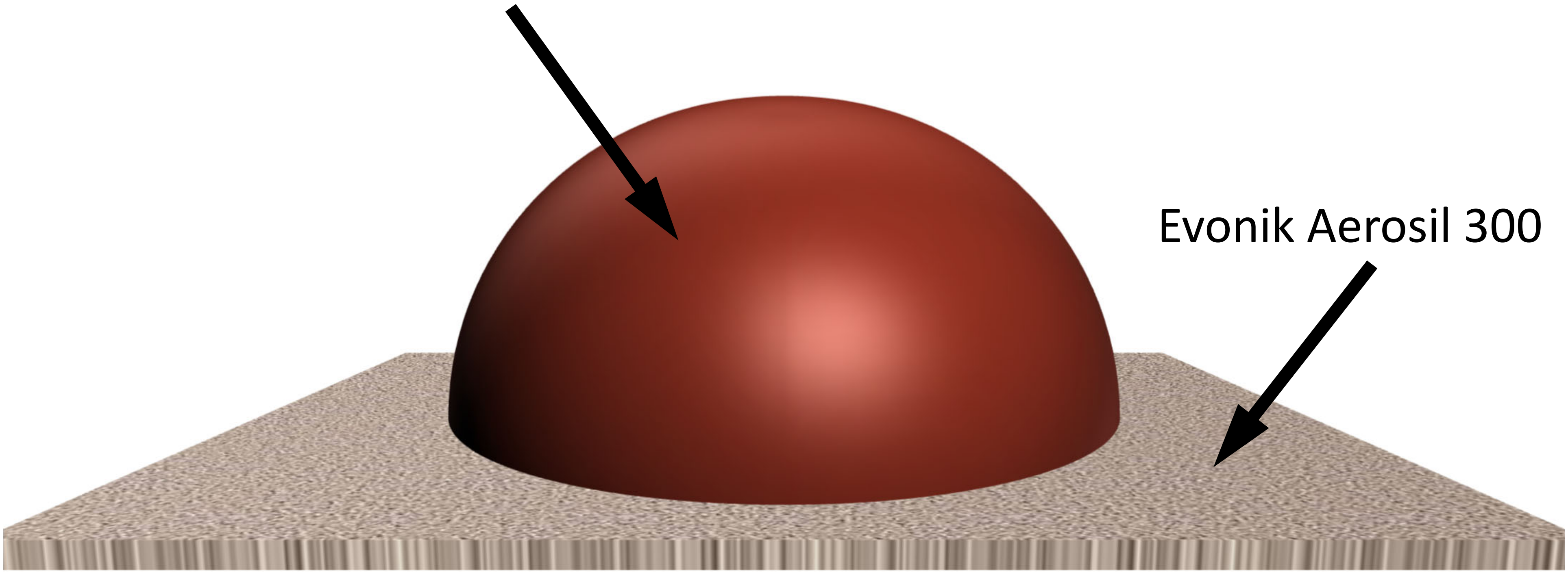
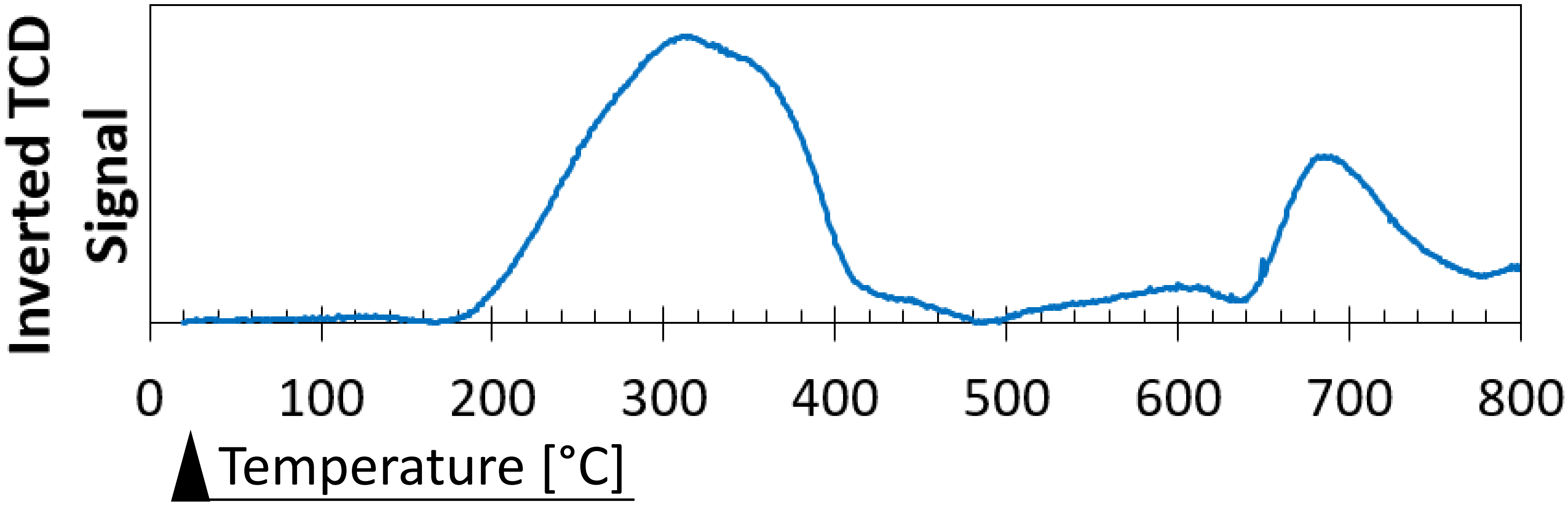
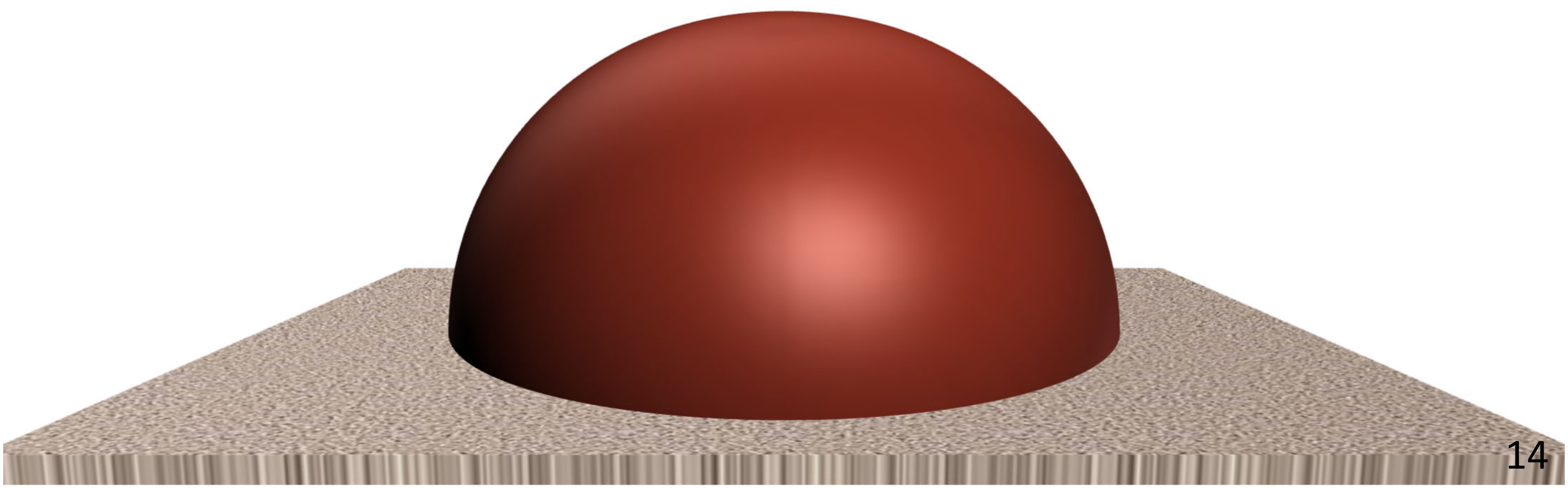
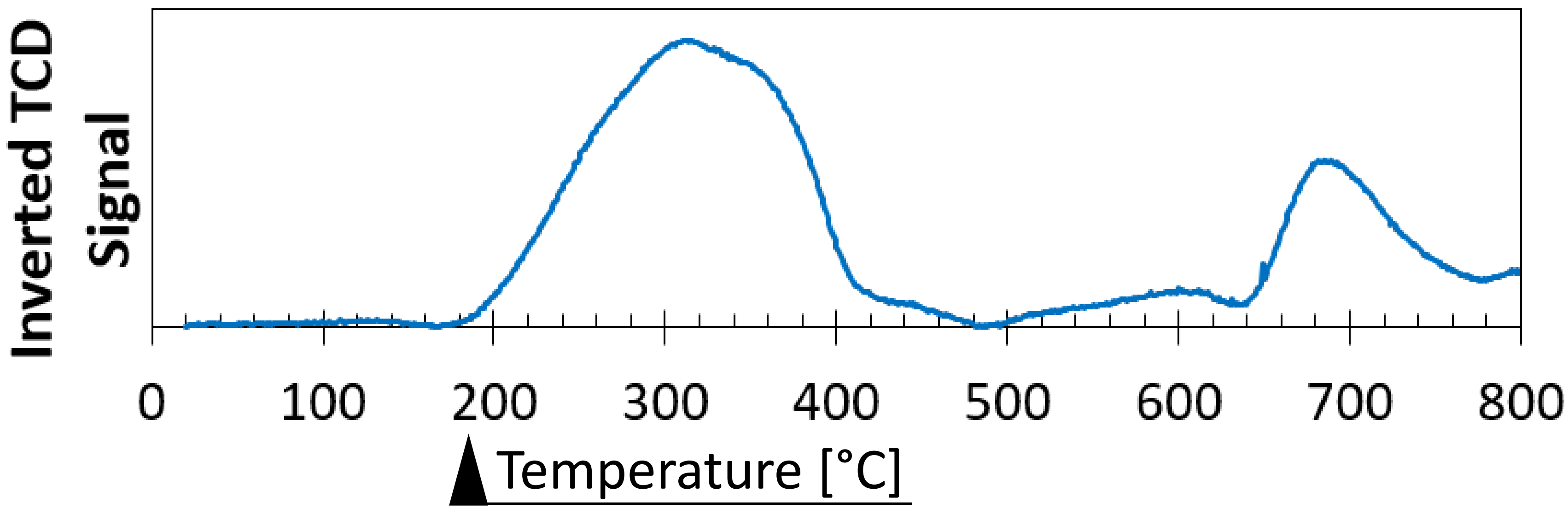
Temperature Programmed Reduction (TPR)

Conditions: 10 °C / min, 50 sccm 10% H_2 in Ar




Inverted TCD Signal
0
100
200
300
400
500
600
700
800
Temperature [°C]




Inverted TCD Signal
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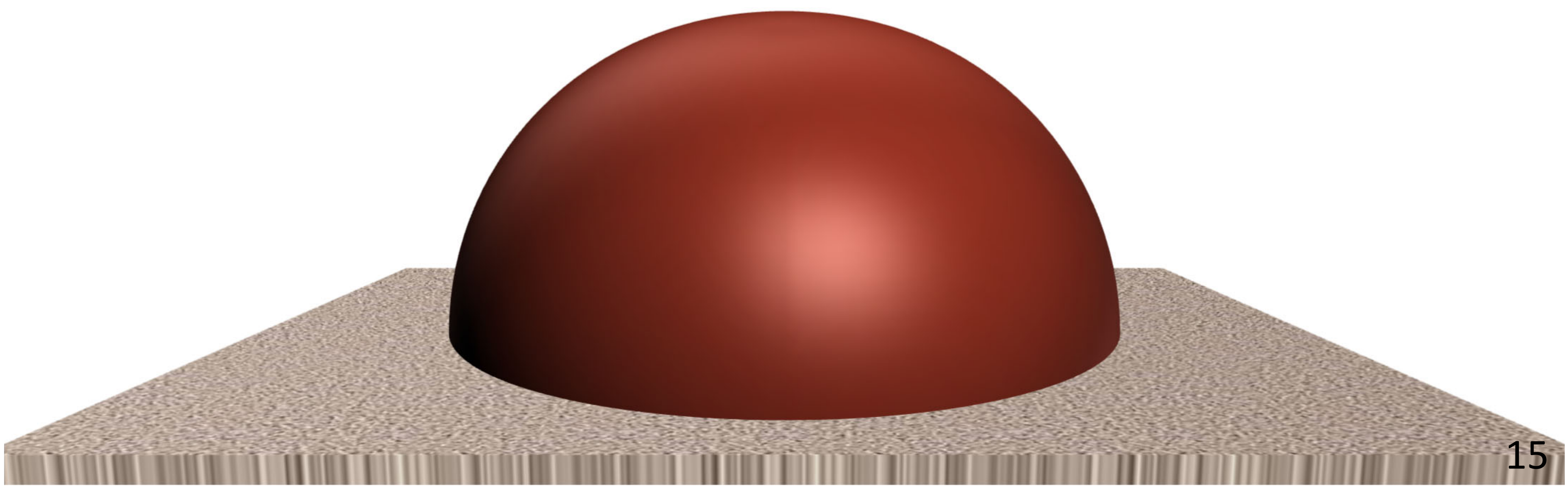
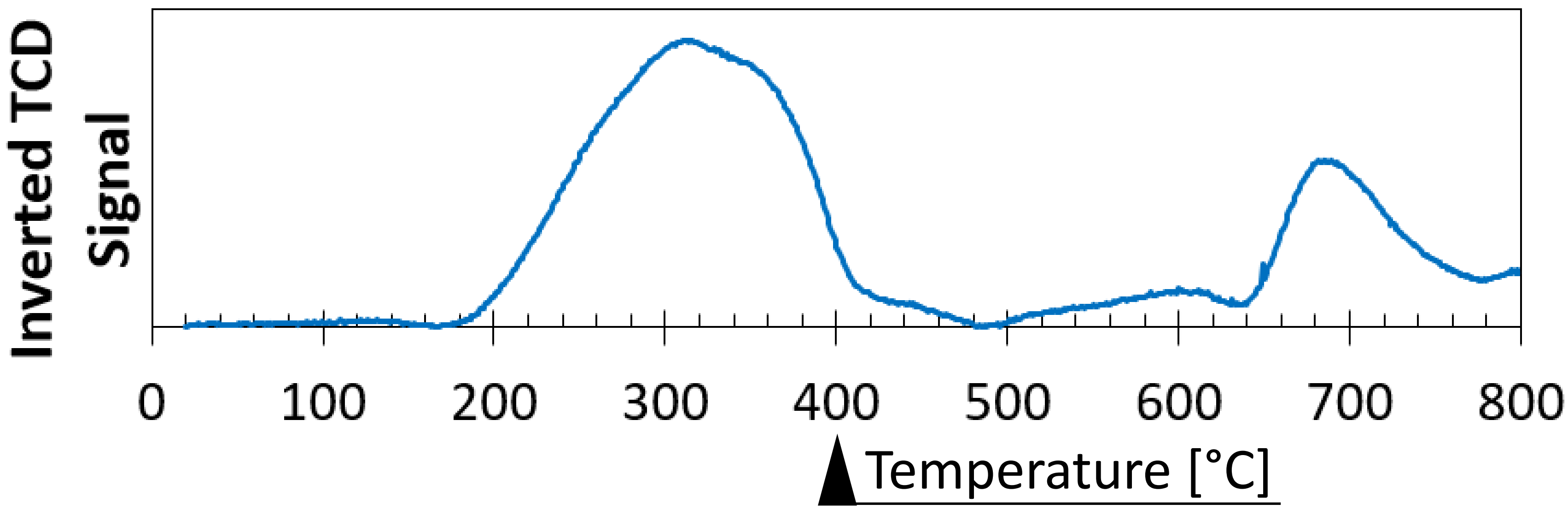
Temperature [°C]




Inverted TCD Signal
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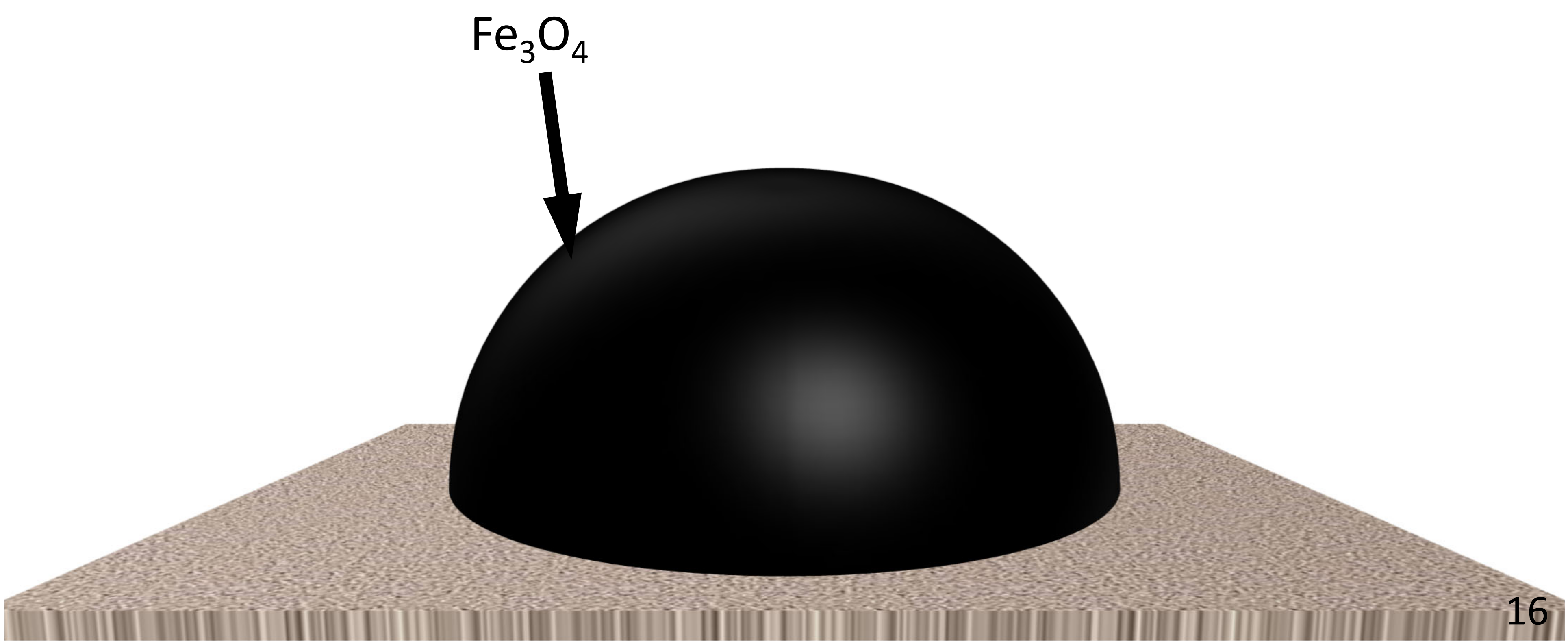
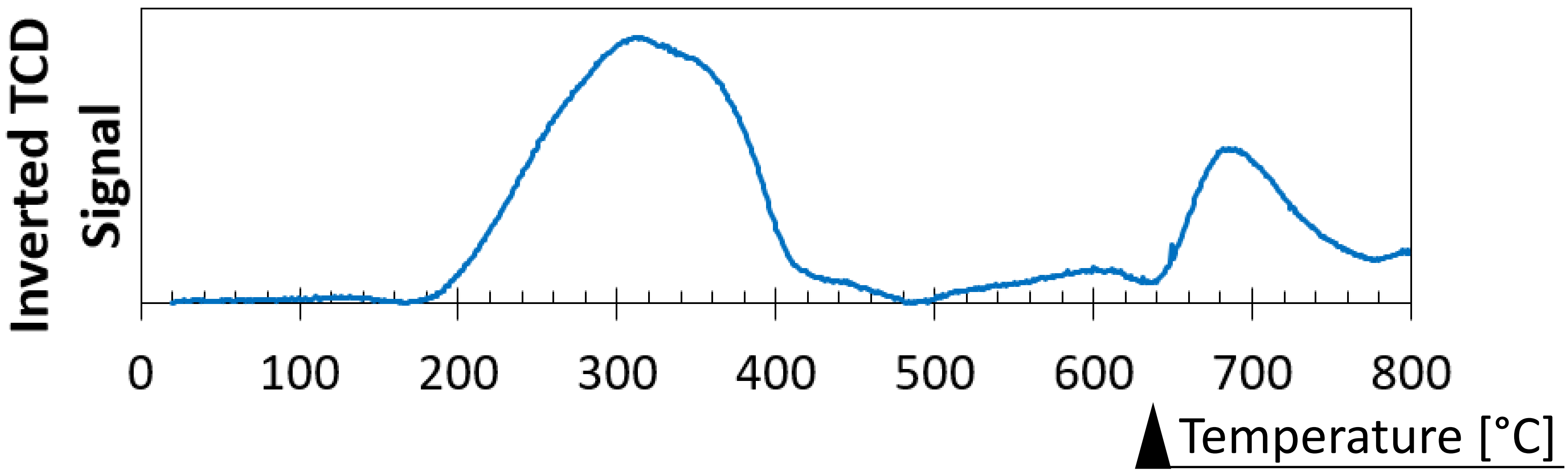
Temperature [°C]


Fe_3O_4


Inverted TCD Signal
0
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300
400
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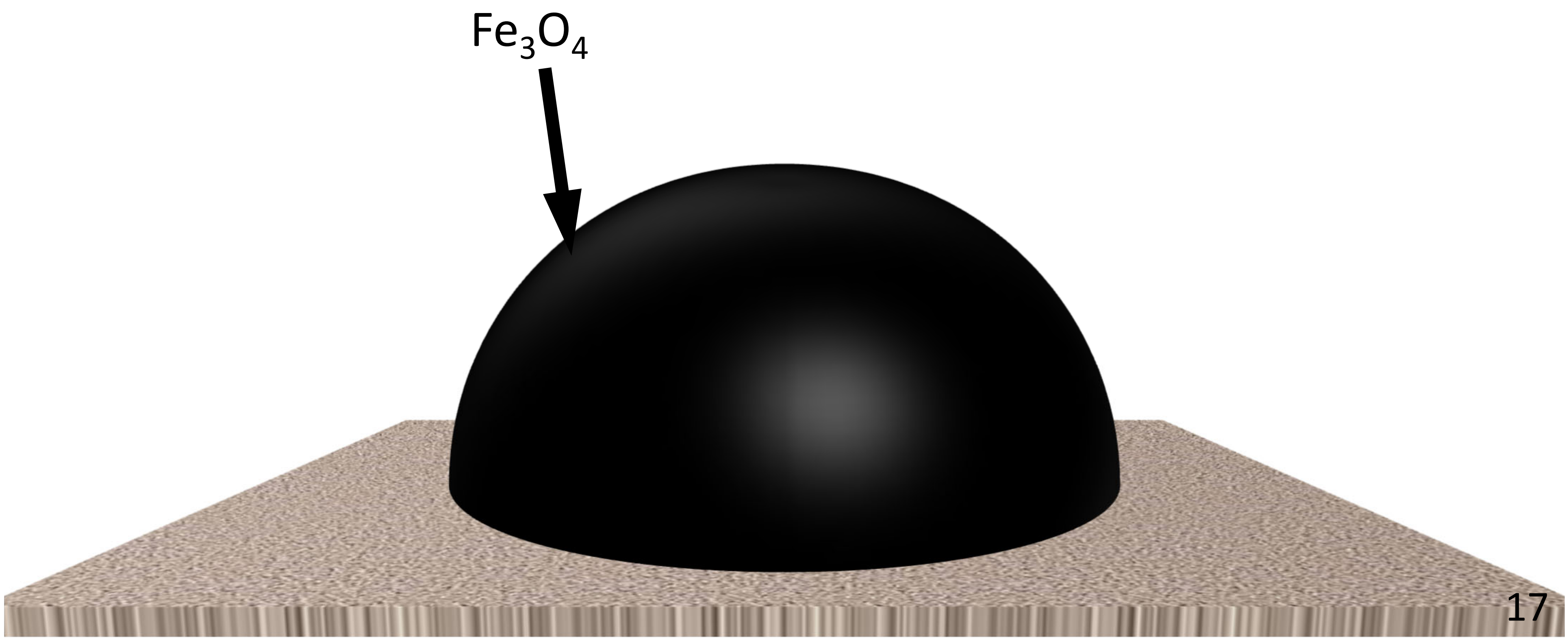
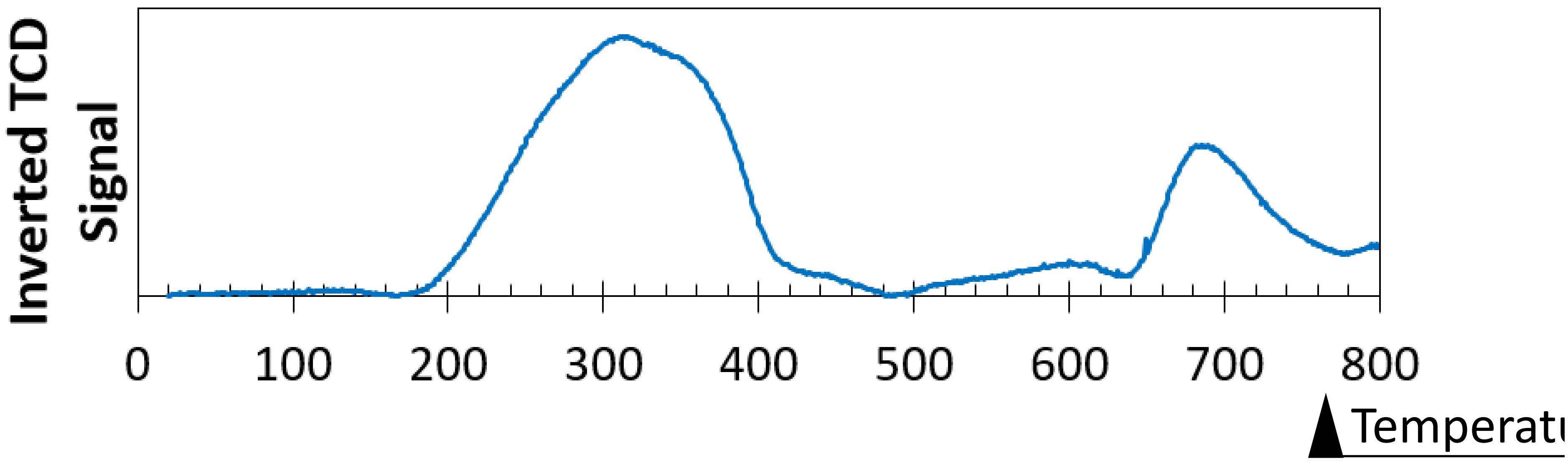
600
700
800
Temperature [°C]


Fe3O4


Inverted TCD Signal
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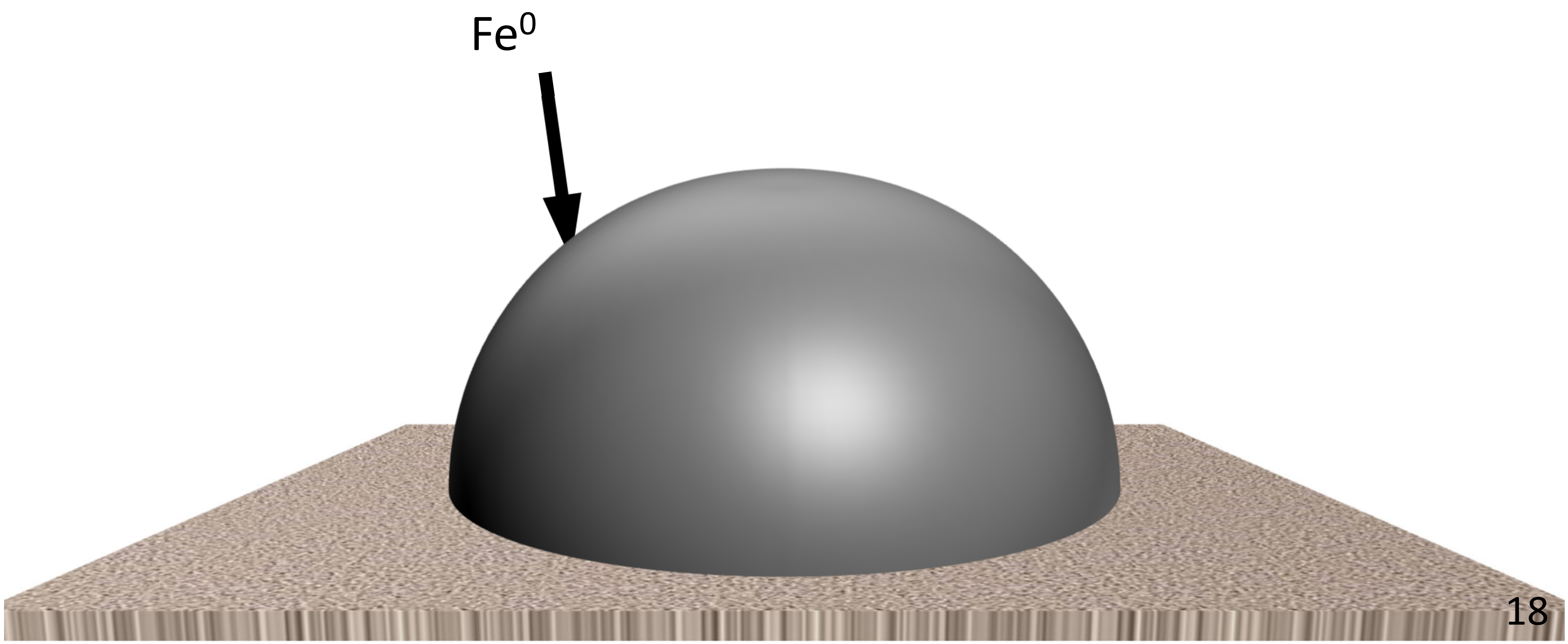
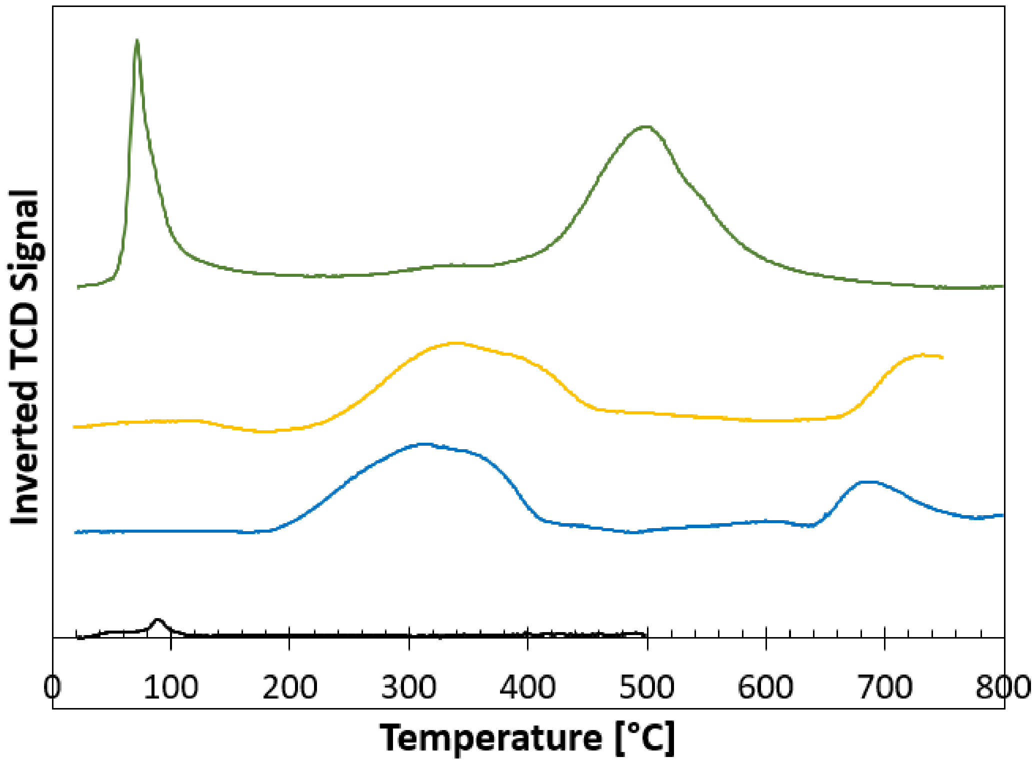
Temperatu


Fe^0

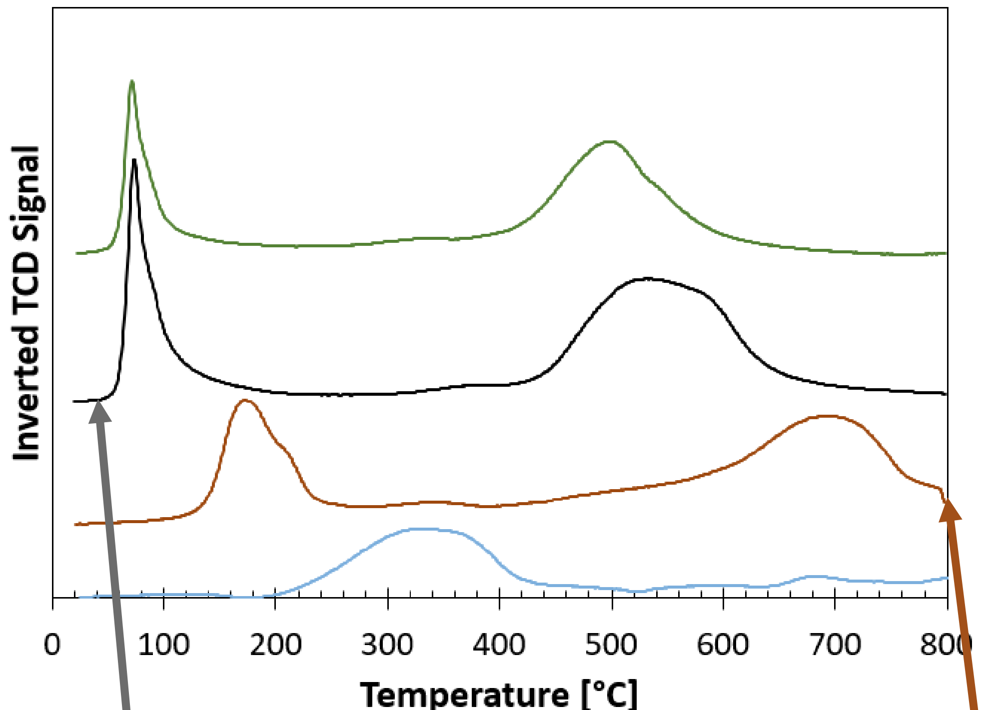
Pd-Fe interaction: TPR



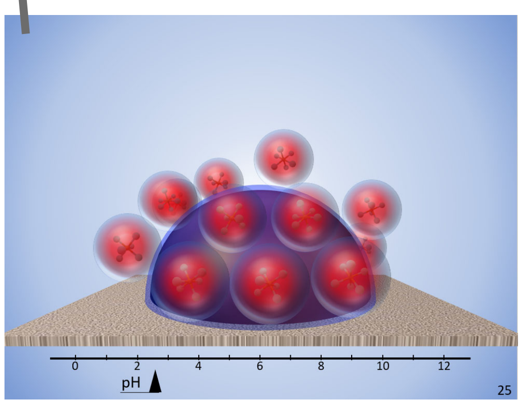
Sample	Pd [mg]	Fe_2O_3 [mg]
0.17%Pd / 13.7%Fe_2O_3 / A300	0.35	28.0
13.7%Fe_2O_3 / A300 + 1.8%Pd / A300	0.35	27.2
13.7%Fe_2O_3 / A300	0	28.0
1.8%Pd / A300	0.35	0

- Physically mixing samples in the TPR does not aid in reduction
- SEA to put Pd on Fe_2O_3 greatly aids reduction

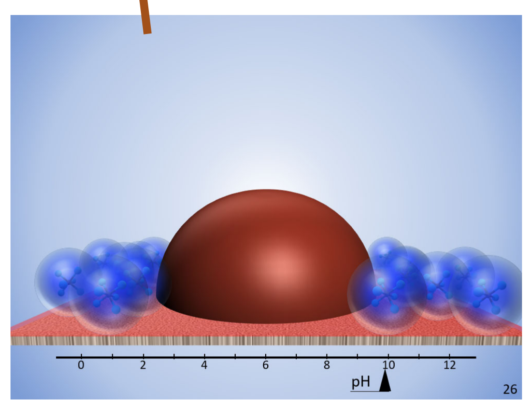
H_2 Spillover vs. Pd proximity



Sample	Pd [mg]	Fe_2O_3 [mg]
0.17%Pd / 13.7%Fe_2O_3 / A300 (8 nm)	0.35	28.0
0.24%Pd / 13.3%Fe_2O_3 / A300 pHf **3.06**	0.48	28.0
0.23%Pd / 13.3%Fe_2O_3 / A300 pHf **9.90**	0.46	26.4
13.3% Fe_2O_3 / A300	0	26.3

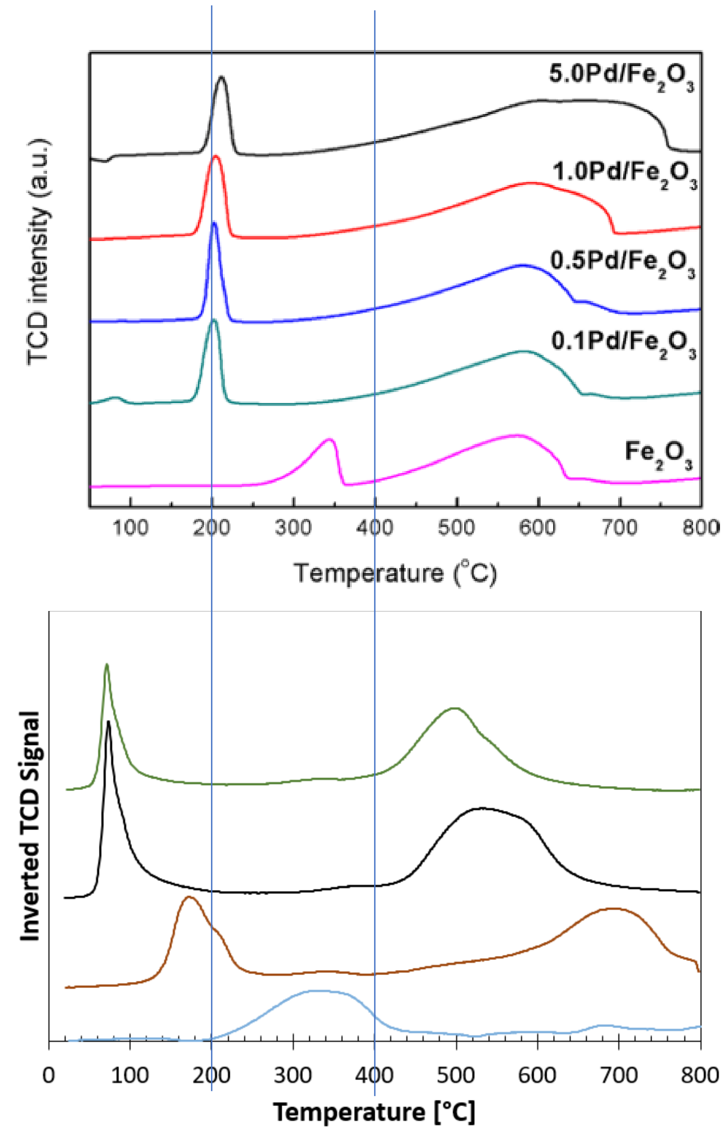


Vs.



TPR comparison with Literature[12]

- SEA prepared Pd catalysts (1.72 wt% Pd on Fe_2O_3) show the first reduction peak at 130 °C lower than 0.1 to 5wt% catalysts prepared by incipient wetness impregnation
- Evidence of stronger metal-metal interaction
- Note: the initial Fe particle sizes are different. Our silica supported Fe_2O_3 particles are 5nm, their unsupported Fe_2O_3 particles are 20nm.



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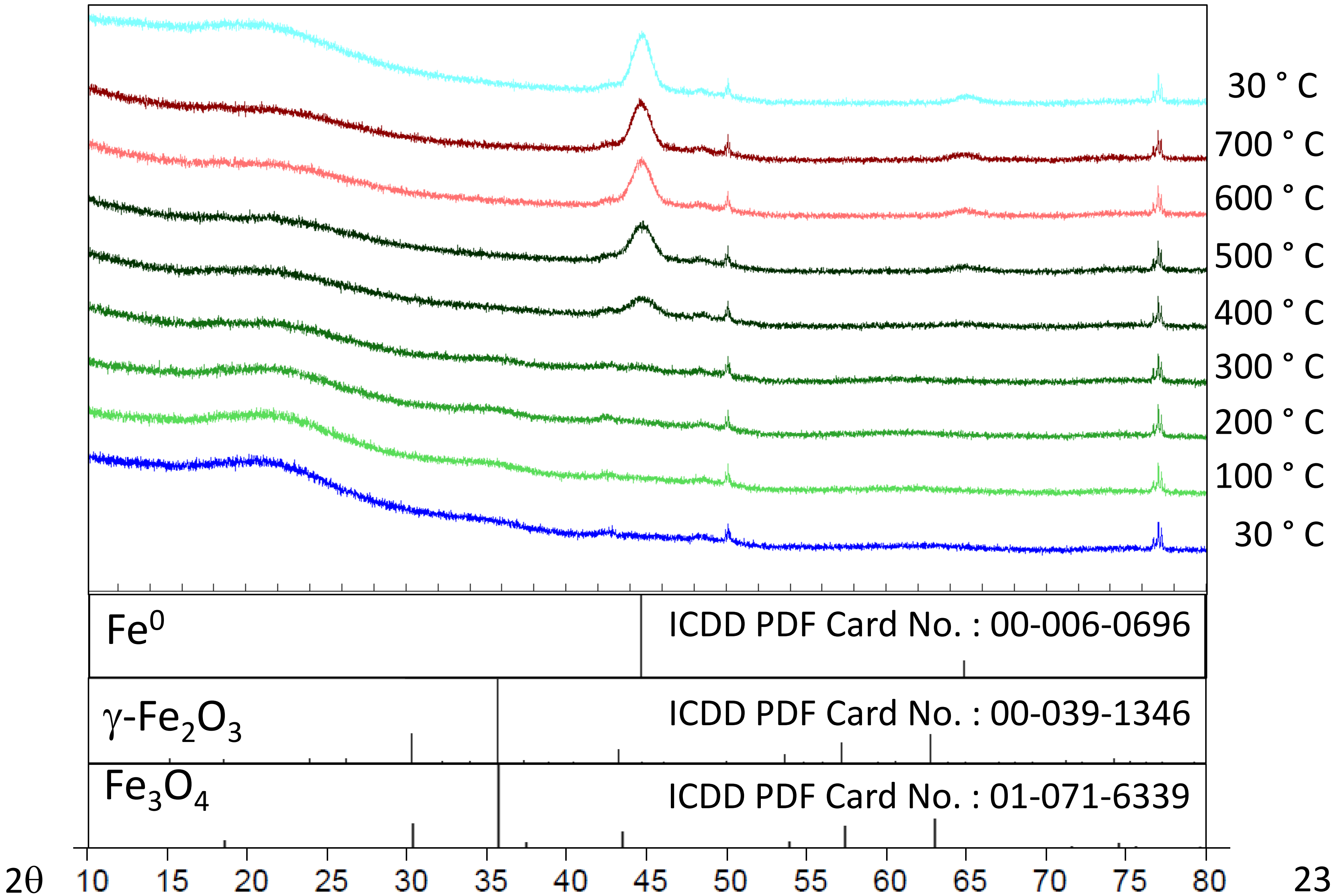
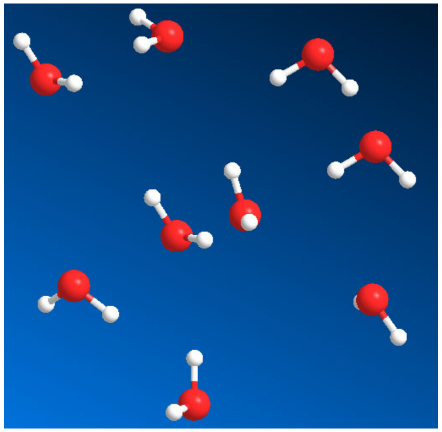
In-Situ XRD: 0.24%Pd/13.3%Fe_2O_3/A300



Catalytic Activity

- This series of catalysts completely oxidizes under reaction conditions with H_2O as solvent
- This series of catalysts undergoes majority oxidation under reaction conditions with hexadecane as solvent
- Liquid-phase kinetic data will need to wait for more stable catalysts



Conclusions

- Pd-Fe prepared with SEA shows enhanced interaction in TPR
- The current array of catalysts oxidizes under reaction conditions
- Future work requires further catalyst design and synthesis for enhanced stability during liquid-phase HDO

Acknowledgements

- National Science Foundation IGERT Grant
- Smartstate Center of Catalysis for Renewable Fuels – University of South Carolina
- JR Group
- Dr. Monnier Group
- Dr. Lauterbach Group

Questions?

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2. Huber, G. W.; Iborra, S.; Corma, A., Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. *Chemical Reviews* **2006,** *106* (9), 4044-4098.
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12. Hensley, A. J.; Hong, Y.; Zhang, R.; Zhang, H.; Sun, J.; Wang, Y.; McEwen, J.-S., Enhanced Fe2O3 reducibility via surface modification with Pd: Characterizing the synergy within Pd/Fe catalysts for hydrodeoxygenation reactions. *ACS Catalysis* **2014,** *4* (10), 3381-3392.