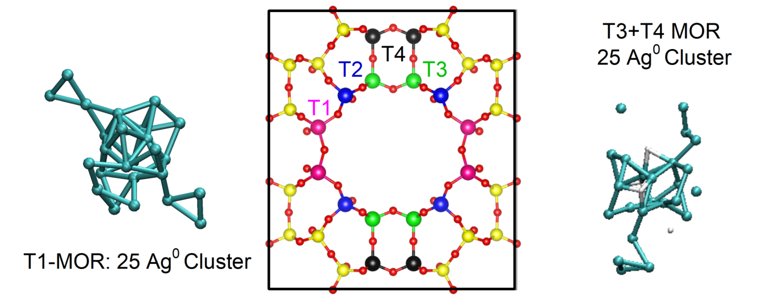
SAND2022-8622C

Energetics and Structure of Ag-Water Clusters formed in Si/Al-Mordenite



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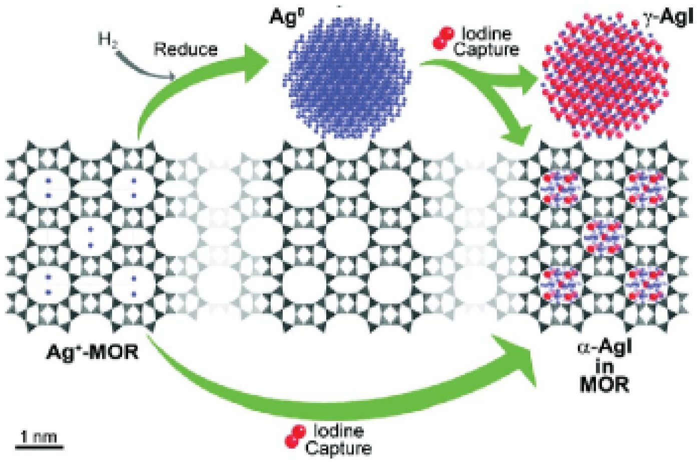
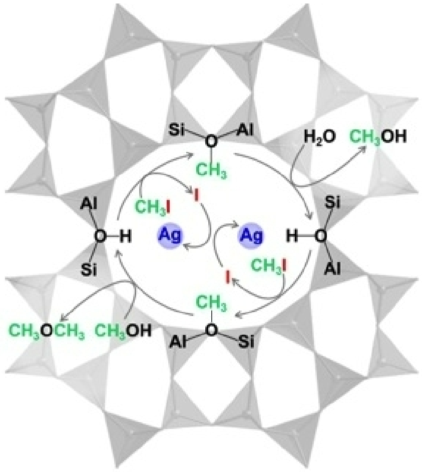
Introduction

- Functional behavior of metallic nanoparticles is controlled by their size and shape.
- Zeolitic supports confine particle growth to control the resulting nanoparticles.
- Zeolite supported metal clusters have applications including catalysis, gas separation, and iodine capture.
- In-situ pair distribution function methods identified multistep mechanisms of cation reduction, cluster formation, and nanoparticle growth for Ag formation in mordenite and role in iodine capture.



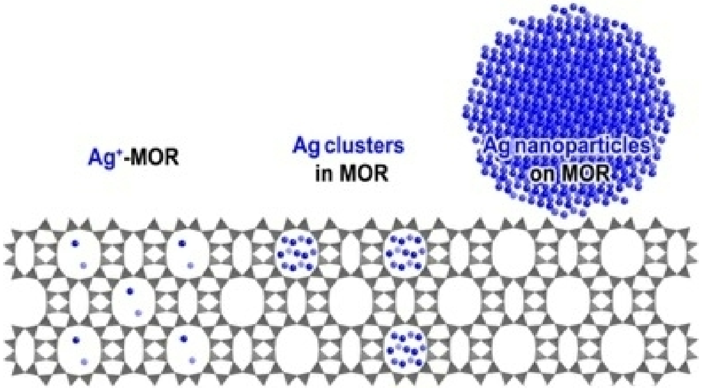
Chemical loading, reduction, and activity of AgI in MOR

Chapman, Chupas & Nenoff (2010) J. Am. Chem. Soc. 132(26) 8897-8899.



Ag-MOR + CH3-I gas adsorption mechanism

Nenoff , et al. Micro. Meso. Mater. 200 (2014): 297-303.



PDF study of Ag nanoparticle formation and migration

Zhao et al. J. Phys. Chem. Lett. 2.21 (2011): 2742-2746.

- How many Ag atoms can fit within MOR porosity?
- How does confinement alter the structure of the Ag^0 clusters?
- How does the placement of Al in the mordenite structure control Ag^0 nanocluster formation?

Molecular scale modeling can provide fundamental structural insight to answer these questions.

Refs: Nenoff, Rodriguez, Soelberg, & Chapman (2014). *Microporous Mesoporous Mater.*, *200*, 297-303, Zhao, Nenoff, Jennings, Chupas, & Chapman (2011). *J. Phys. Chem. Lett.*, *2*(21), 2742-2746.

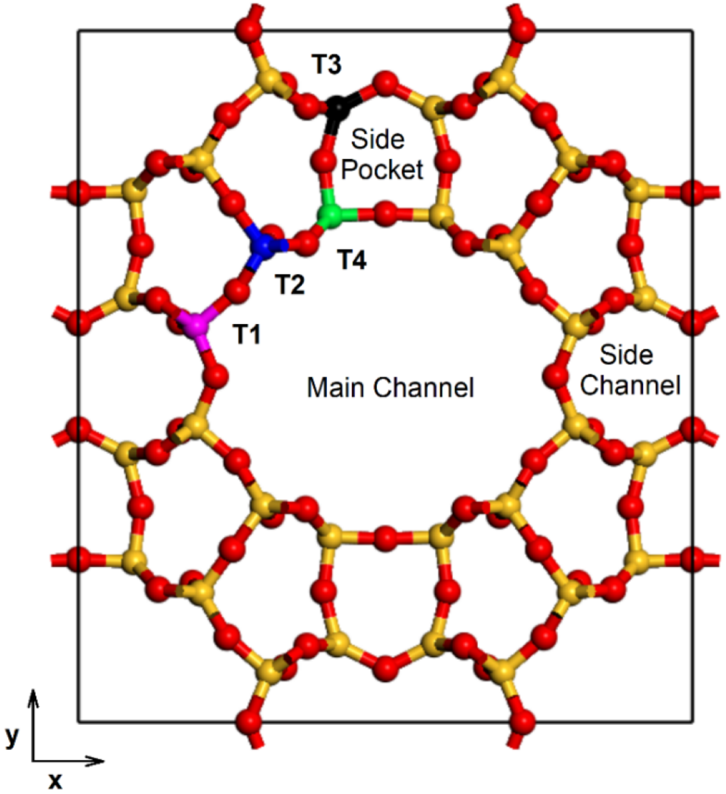
Computational Methods

Overview
- Periodic density functional theory (DFT).
- Vienna *ab initio* Simulation Package (VASP).

Mordenite Structure Models
- 152 atom MOR framework structures (a=17.60 Å, b=20.32 Å, c=7.50 Å, $\alpha=\beta=\gamma=90^o$).
- SI-MOR structure plus Al/Si-MOR with Al substitution on the T1, T2, and T3+T4 positions with 5:1 Si:Al ratio.

Sava, D. F., Garino, T. J., & Nenoff, T. M. (2012). Ind. Eng. Chem. Res., 51(2), 614-620.

- Protons are used for charge balance.



Clusters: Water, silver, and water+silver clusters were introduced into the main channel

Cluster Sizes					
Ag	5	10	15	20	25
H_2O	5	10	15	20	25
Ag+H_2O	3+3	5+5	8+8	10+10	12+12

- Structural relaxation via a simulated annealing procedure

Hoffman, A., DeLuca, M., & Hibbitts, D. (2019 J. Phys. Chem. C, 123(11), 6572-6585.

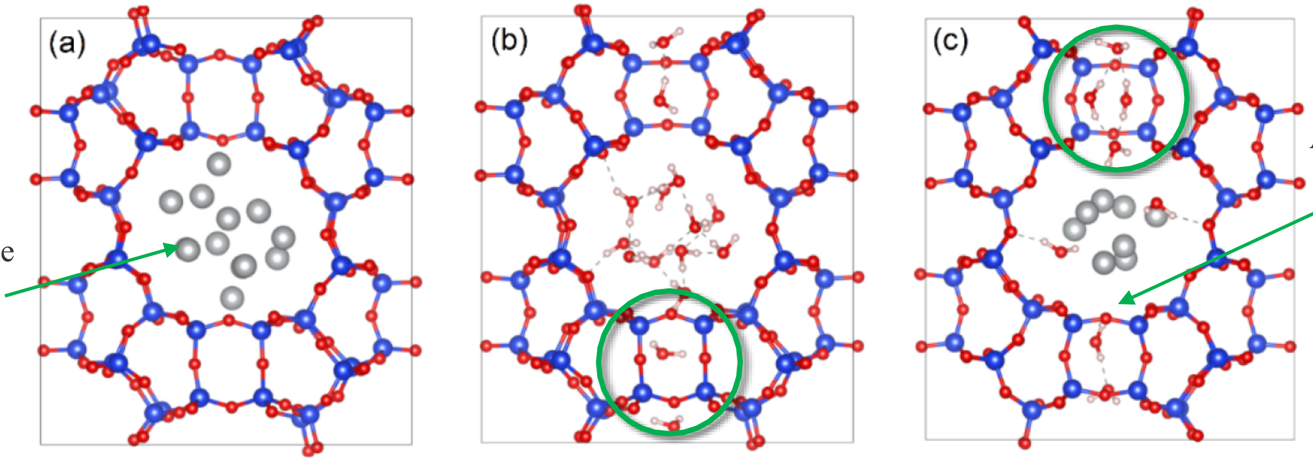
Note: T3+T4 occupancy is higher than seen experimentally, in violation of the Löwenstein rule.
- Allows for investigation of a consistent Al position in the framework.
- Opportunity to identify how Al substitution impacts Ag cluster formation.
- Stable zeolites that violate the Löwenstein rule have been reported.

Fletcher, R. E., Ling, S., & Slater, B. (2017). Chem. Sci. 8(11), 7483-7491.

Additional Details
- MOR framework from the Database of Zeolite Structures
- Energy convergence = 10-6eV, Energy Cut-Off = 400 eV
- PBE Exchange Correlation Functionals and gamma point Brillouin zone sampling
- DFT-D3 long-range dispersion interactions

Stability of Ag^0 + Ag^0:H_2O Clusters in Mordenite

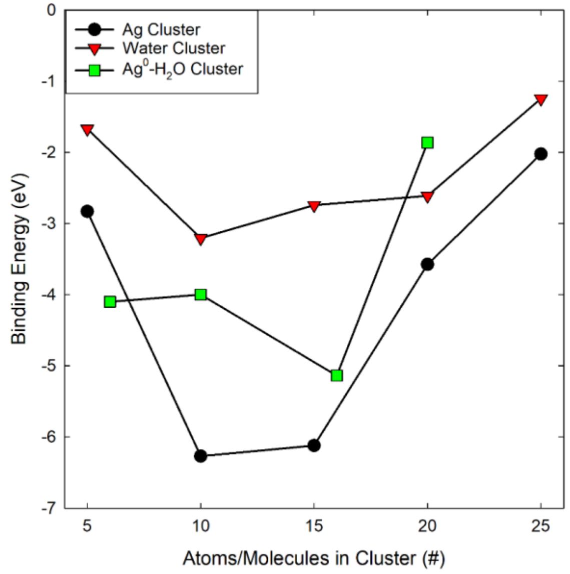
- Calculated a drive towards formation of 10-15Ag^0 clusters in the Mordenite main channel.
- Mixed Ag^0+nH_2O clusters are generally less energetically favorable then Ag^0 clusters.



Ag atoms in the main pore

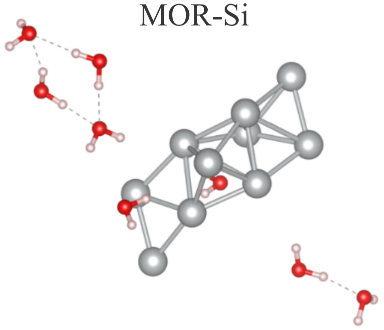
Ag atoms in the main pore + water in side channels

Water molecules in main pore + side channel

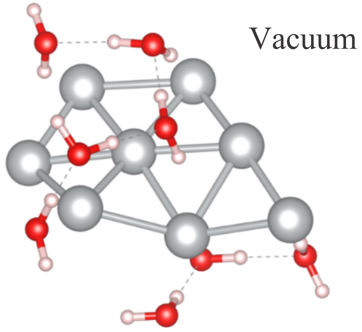


- Clusters confined in Mordenite (MOR) structure have larger surface areas than those in vacuum.
- The Ag-Ag distance increases as the cluster grows from 5Ag^0 to 25Ag^0.
- PDF and identified changes in Ag-Ag distance due to cluster size.

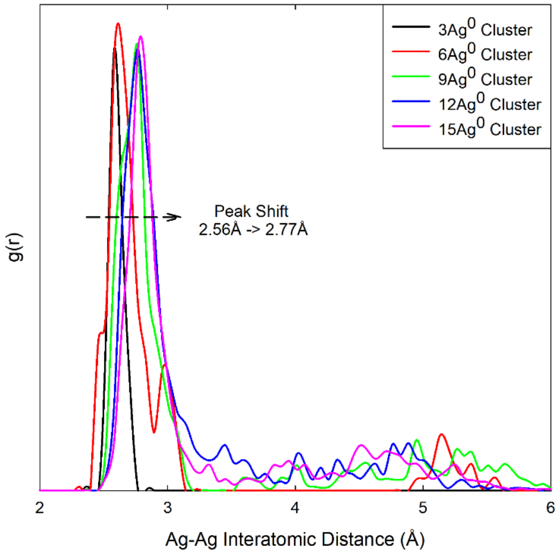
MOR-Si



Vacuum

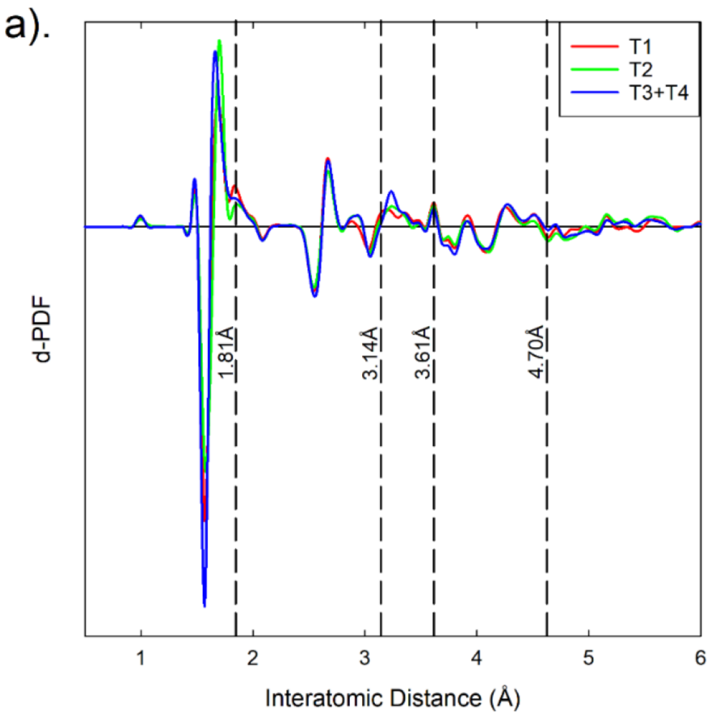


		Density (g/cm³)	Surface Area (Å²)	Energy (eV/atom)
8Ag^0–8H_2O	Vacuum	7.917	279.50	-4.119
	Si-MOR	8.507	296.82	-4.108



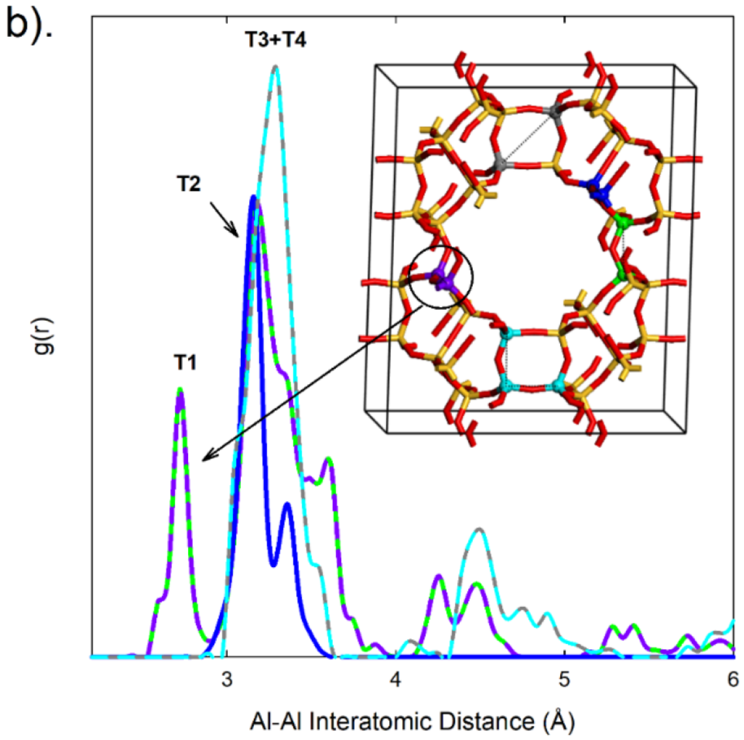
Al/Si MOR structure model and PDF

- Pair distribution function (PDF) data were used to identify differences in T1, T2, and T3+T4 structures.
- Calculated from 1 ps of *ab initio* molecular dynamics (AIMD) trajectory with a 0.5 fs time step.
- Subtle differences in PDF in the range (4.2-4.7 Å) due to Al-Al interactions, but challenging to separate based on overlapping peaks.



- Differential PDF – provides more detail on changes in the structure.
- Al···Al PDF also identifies Al locations for T1, T2, and T3+T4 positions in the structure.

The inclusion of Al atoms in the MOR structure results in differences in the PDF that are most apparent in the Al···Al PDF results.

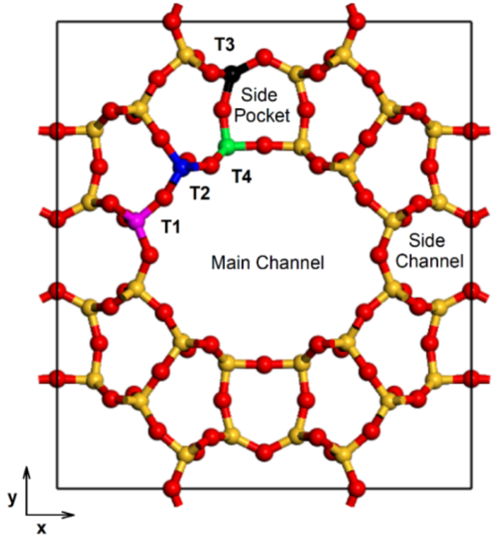


PDF Peak	Si-MOR	Al-MOR
Tetrahedron peaks	1.65Å	1.70Å
Al···O/Si···O	Shoulder at 1.81Å	
Si···Si	3.14Å	3.30Å

O-T-O bond angles in Al-MOR

Bond angle distributions (BAD) identify changes in the of the O-T-O angles.

The wider O-T-O BAD data allows for more variation in the zeolite structure, can may enable easier movement of the Ag^0 cluster to the surface.



Impact of Clusters

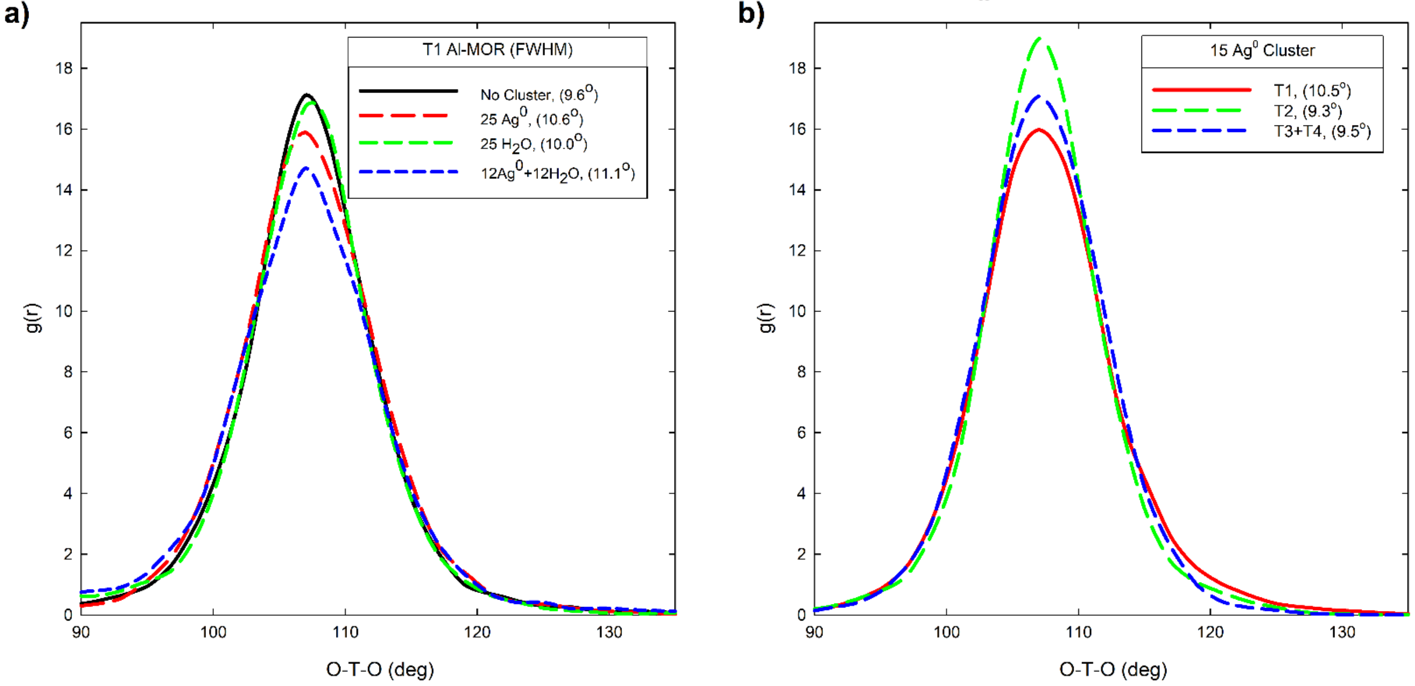
- H_2O clusters do not change the flexibility of the framework → adapt to existing pore space.
- Ag and Ag+H_2O clusters result in broader O-T-O distribution → Ag^0 clusters have preferred geometries.

Chen, M., Dyer, J. E., Li, K., & Dixon, D. A. (2013). *J. Phys. Chem. A*, *117*(34), 8298-8313.

Impact of Al-Position

- Widest variation for T1-MOR (link between side and main channel).
- Smallest variation for T2-MOR (inside main channel).

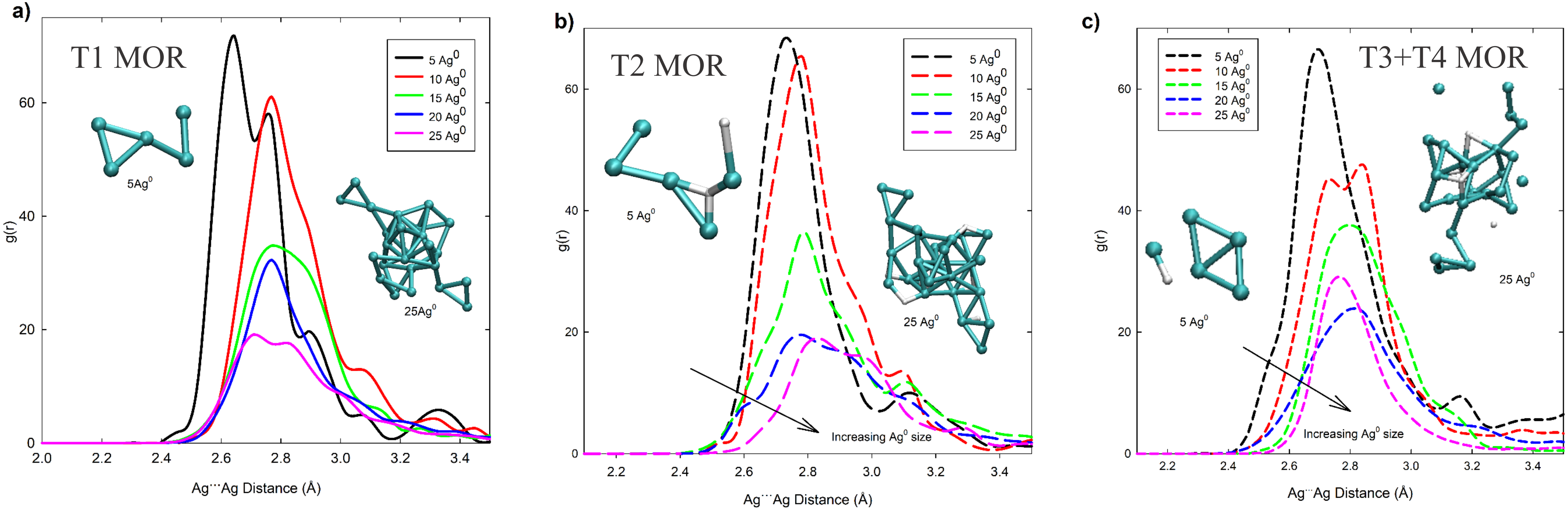
T1-MOR with H_2O+Ag^0 clusters will exhibit the broadest O-T-O BAD spectra, and therefore the easiest escape of Ag^0 particles



Ag^0 clusters in Al-MOR structures.

- Shift to longer Ag···Ag interatomic distances (2.6Å to 2.8Å) as Ag^0 cluster size increases (across all Al-MOR structures).
- Shorter Ag···Ag interatomic distances (~2.4Å) due to hanging Ag-Ag bonds.
- T2 MOR and T3+T4 MOR incorporate H-atoms into the cluster .
- Stability of Ag$_x$H bonds have been previously reported.

Kuang, X., Wang, X., & Liu, G. (2011). *Structural Chemistry*, *22*(3), 517-524.



What is the impact of the charge on the Ag cluster?

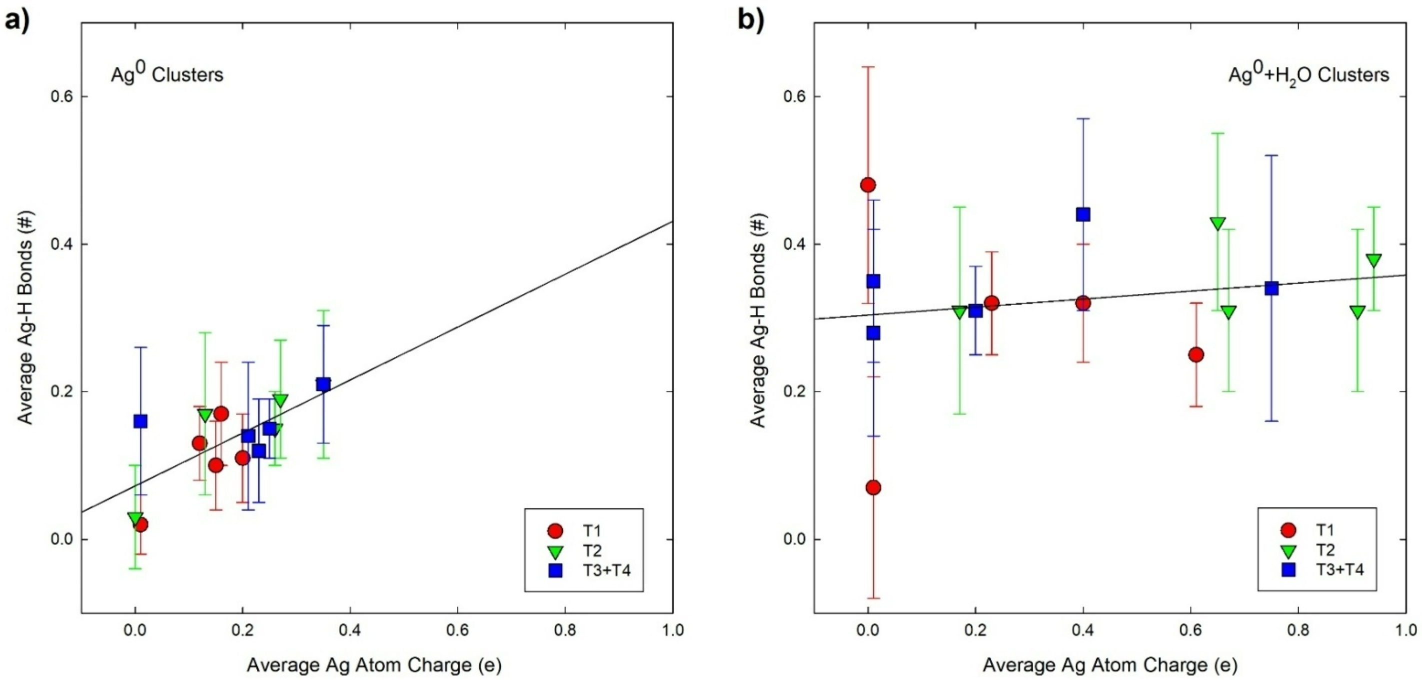
Formation of Ag-H bonds on Ag^0 clusters.

- Stripping the H from the Al-MOR can form a charged zeolite framework.
- Bader charge analysis used to evaluated change in charge of Ag clusters.
- Ag charge increases with cluster size across all frameworks.

Tang, W., Sanville, E., & Henkelman, G. (2009). *J. Phys. Condens. Matter*, *21*(8), 084204.

Charge of Ag Cluster (e)

Ag	T1	T2	T3+T4	$Ag+H_2O$	T1	T2	T3+T4
5	0.12	0.75	1.04	3+3	1.43	0.92	1.02
10	1.10	0.28	1.56	5+5	0.34	1.90	2.22
15	2.50	2.53	2.24	8+8	1.99	2.46	2.79
20	2.67	4.30	2.30	10+10	3.20	4.26	2.82
25	2.49	4.57	3.33	12+12	3.81	3.73	3.67



- Ag clusters: loose linear relationship between the # of Ag-H bonds and the average Ag charge.
- Ag + H_2O: Higher average Ag charge, no dependence on Ag-H bonds.

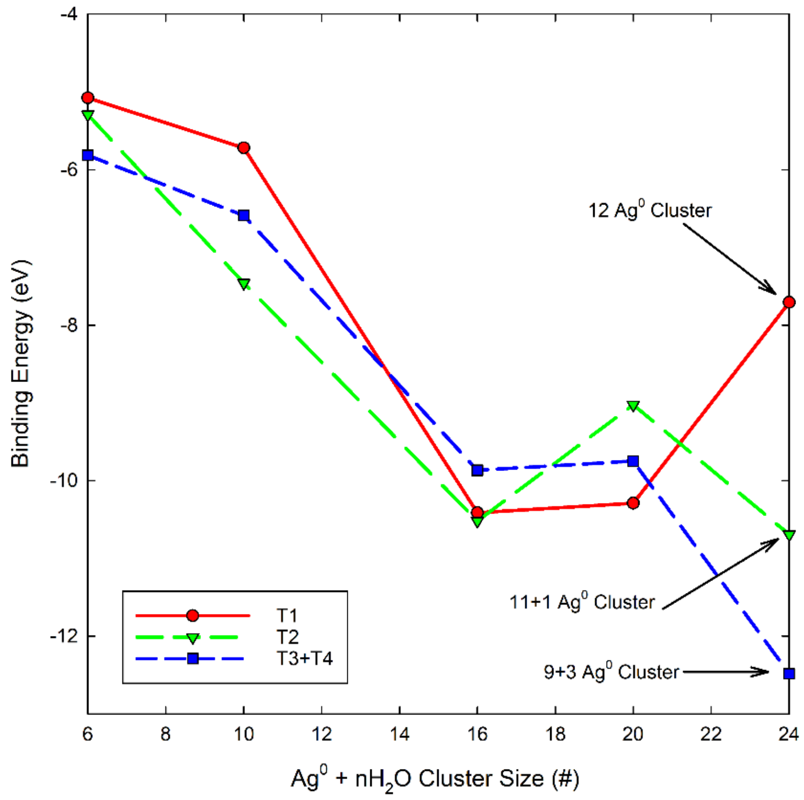
Charged Ag clusters may have challenges escaping the pore due to providing charge balance with the remaining de-protonated MOR framework.

Binding Energy of Ag^0+H_2O Clusters in Al-MOR

- For Ag + H_2O clusters there is a thermodynamic drive for development of 8 Ag + 8 H_2O clusters (across all frameworks).
- For larger cluster sizes results separate:
  - T1 = higher energy, formation of 12 Ag^0 cluster
  - T2 = no energy change, formation of 11 and 1 Ag^0 clusters
  - T3 + T4 = drop in energy, formation of 9 and 3 Ag^0 clusters

Formation of smaller, separated Ag^0 clusters is energetically favorable.

- 9/15 systems had multiple Ag^0 nanoclusters form in the presence of water.
- Most common Ag^0 size was an isolated Ag atom.
- Smaller clusters are more easily formed in T2 and T3+T4 MOR structures.



Initial Cluster Size	Al-MOR		
	T1	T2	T3+T4
3 Ag^0+3 H_2O	2+1	2+1	3
5 Ag^0+5 H_2O	5	5	4+1
8 Ag^0+8 H_2O	8	7+1	5+2+1
10 Ag^0+10 H_2O	10	8+1+1	9+1
12 Ag^0+12 H_2O	12	11+1	9+3
Avg + SD	6.33±4.03	3.80±3.52	3.80±2.89

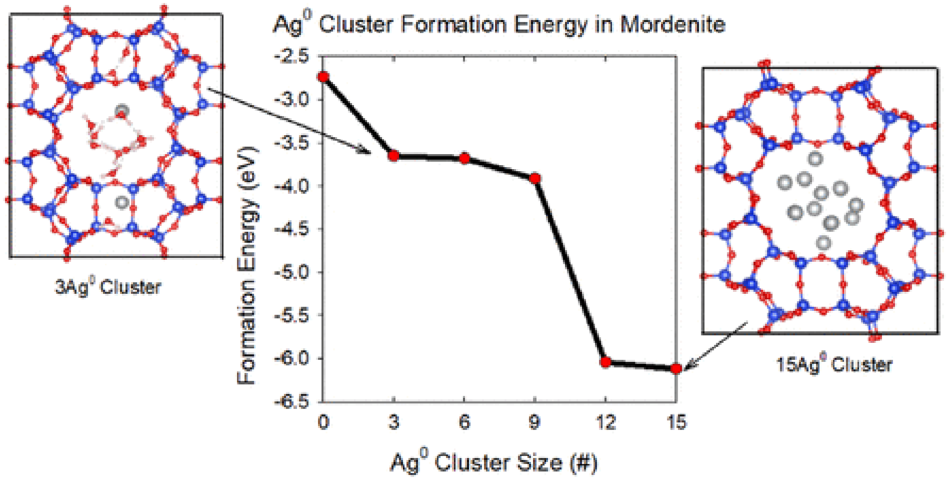
T2 and T3+T4 MOR are more likely to form small Ag^0 clusters in the presence of water that can diffuse to the surface.

Conclusions

The formation of Ag^0 nanoclusters in Al-MOR requires a balance of stable MOR structures, charge balance, and diffusivity.

Density functional theory (DFT) simulations were used to investigate changes in the structure, charge, and energy of the Ag-zeolite systems changes with:

1. The composition (Ag^0, H_2O, Ag^0+H_2O) of the clusters in the main pore.
2. The location of Al in the MOR framework (T1, T2, T3+T4).



- 15 Ag^0 particles are the most stable and confined silver nanoparticles have larger surface areas than unconfined clusters.
- T1-MOR is predicted to have the best combination of high variation in O-T-O bond angles and low Ag charge for formation of neutral Ag clusters.
- T3+T4 MOR formed the smallest average cluster size but is likely to have difficulty being synthesized.
- T2-MOR has the least favorable properties for Ag nanocluster formation.
- The presence of water results in more framework flexibility and the formation of smaller Ag nanocluster that can escape the main pore.

Overall, T1, T3, and T4 position provides beneficial effects through framework flexibility and changes in nanocluster size or charge that can be leveraged for design of zeolite for formation of metallic nanoclusters.

Acknowledgement

Funding

The work was supported as part of the UNCAGE-ME and GENESIS, Energy Frontier Research Centers funded by the U.S. Department of Energy, Office of Science

D. Jon Vogel, PhD
Susan E. Henkelis, PhD
Sandia National Laboratories

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Co-Authors

- Karena Chapman (Stony Brook University)
- Tina Nenoff (Sandia National Laboratories)

For more information:

1. Rimsza, J.M., K.W. Chapman, and T.M. Nenoff. "Energetics and structure of Ag–water clusters formed in mordenite." *J. Phys. Chem. C* 124.8 (2020): 4517-4524.
2. Rimsza, J.M., K.W. Chapman, and T.M. Nenoff. "Influence of Al location on formation of silver clusters in mordenite." *Micro. Meso. Mater.* 327 (2021): 111401.

Tuesday at 5pm in Poster Session 2

“Competitive Adsorption and Reactivity of Acid Gases in Rare Earth Metal Organic Frameworks” by Matthew Christian

Thursday at 5pm in Poster Session 3

“Gas Interactions with CC13-based Type 2 Porous Liquids” by Jessica Rimsza

Friday at 12pm in Session 12 (Room 4)

“Near-Zero Power Zeolite and MOF based Sensors for NO_2 Detection” by Tina Nenoff