Silver Clusters in Zeolites: Structure, Stability and Photoactivity

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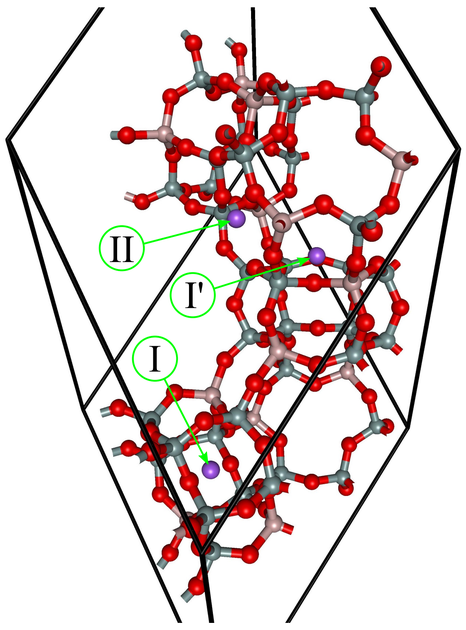
Introduction

- Small clusters of several silver atoms can be formed in silver-exchanged zeolites by partial reduction.[1]
- Fluorescence of heat-treated silver-exchanged zeolites has been recently investigated for the potential use as UV–visible converters.[2]
- The identity of silver particles in zeolites (size, structure, location, charge) has been an open question for a long time.
- Formation of the linear Ag_3^{n+} cluster inside a double-6-ring (D6R) of faujasite has been suggested.[3]
- Electronic charge-transfer transitions from the framework to the silver clusters have been proposed to explain photoactivity.[4]

Model of Ag–faujasite

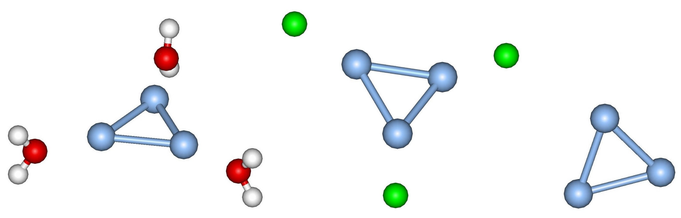


- Periodic model
- Zeolite Y (Si/Al of 2.7)
- Low silver loading (Na/Ag of 3.3)
- Structure of the silver clusters was investigated by geometry optimization at the DFT level.
- Redox stability of the silver clusters was evaluated assuming the reduction by water

$$\tfrac{1}{2}H_2O \rightarrow \tfrac{1}{4}O_2 + H^{\cdot}$$
$$Ag_3^{n+}Y + H^{\cdot} \rightarrow Ag_3^{n-1}H^{+}Y$$

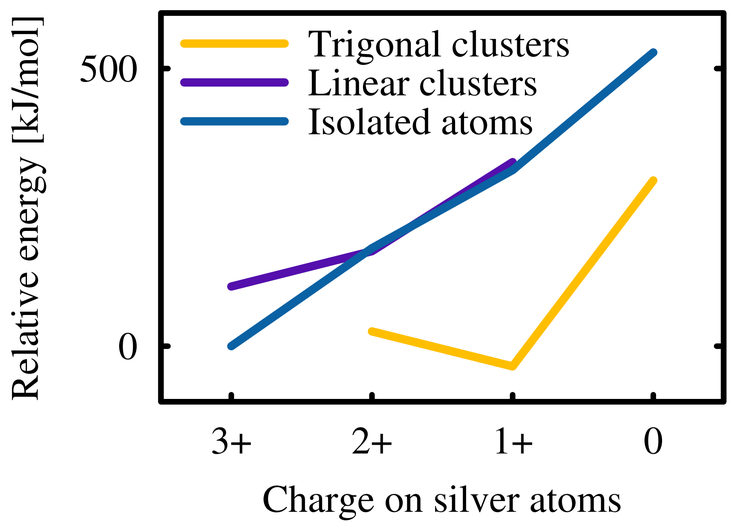
Calculations of excited states

- Reliability of DFT was checked on gas-phase silver cluster models by comparing to accurate post-HF methods.
- Silver clusters with water ligands (to simulate zeolite framework oxygens) and fluoride ligands (to simulate negative charge of the framework), and the bare cluster were investigated.



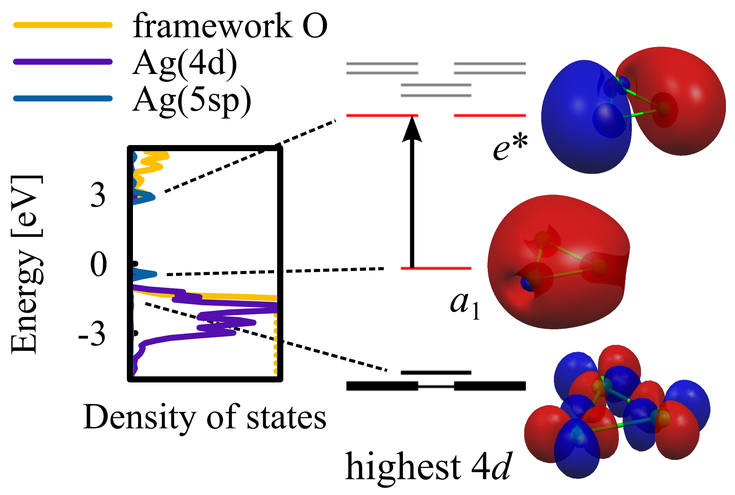
- The post-HF calculations were used to correct transition energies of the silver clusters in zeolite Y calculated by DFT.

Structure and stability of Ag_3^{n+} in zeolite Y

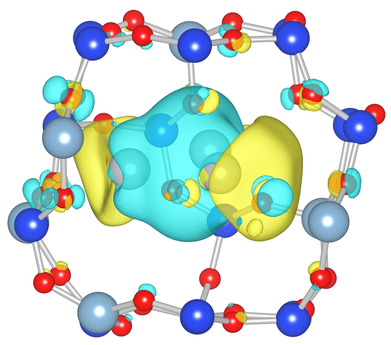


- Prior to reduction, isolated silver cations in zeolite Y are located in sites I (inside the D6Rs).
- Reduction by water leads to the formation of trigonal silver clusters in the sodalite cages, preferably Ag_3^+ which is stabilized by a three-centric two-electron bond.
- Linear silver clusters inside the D6Rs are not the most stable configuration in any reduction degree.

Fluorescence of the trigonal Ag_3^+ cluster

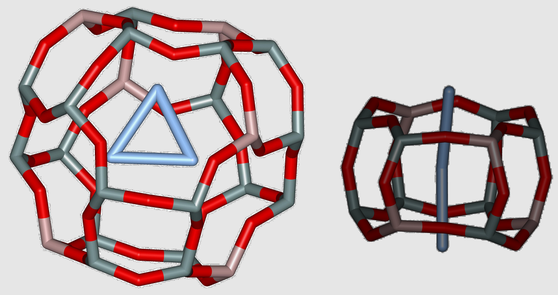


- Comparing the gas-phase orbital diagrams of silver clusters to density-of-state calculations on Ag−Y shows that the zeolite environment does not introduce any new low-lying transitions.
- The lowest lying transition in the trigonal Ag_3^+ cluster is $a_1(5s, \mathrm{HOMO}) \rightarrow e^*(5s, \mathrm{LUMO})$.
- The absorption and emission energy of 3.9 eV and 2.7 eV, respectively, were obtained for the cluster in zeolite Y.

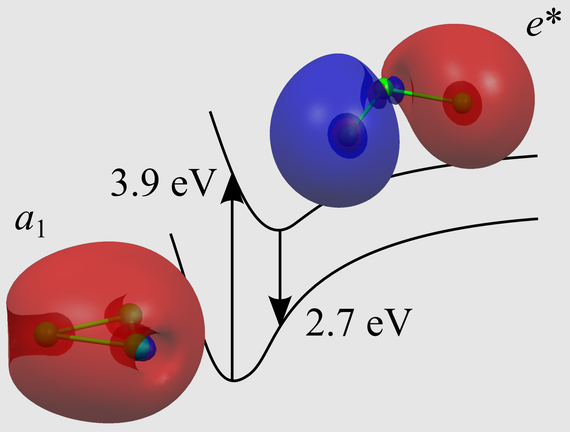


- Electron density difference between the ground state and the excited state shows that the transition is fully localized on the silver cluster.

Conclusions



- Trigonal silver clusters in the sodalite cages are formed upon reduction of silver-exchanged zeolite Y.
- The existence of linear silver clusters in the D6Rs proposed in literature[3] was not confirmed.



- The calculated absorption and emission energies in zeolite Y (left) are comparable to the measured ones of 3.7–4.4 eV and 2.3 eV, respectively.[2]
- These electronic transitions are due to excitations localized on the silver cluster.
- A proposed charge-transfer mechanism from the zeolite to the silver cluster[4] was not confirmed.

References

(1) Sun, T.; Seff, K. *Chem. Rev.* **1994**, *94*, 857.
(2) De Cremer, G.; Coutino-Gonzalez, E.; Roeffaers, M. B. J.; et. al.; *J. Am. Chem. Soc* **2009**, *131*, 3049.
(3) Gellens, L. R.; Mortier, W. J.; Uytterhoeven, J. B. *Zeolites* **1981**, *1*, 11–18.
(4) Calzaferri, G.; Leiggener, C.; Glaus, S.; et. al.; *Chem. Soc. Rev.* **2003**, *32*, 29–37.

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Further information

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