

## The Intrazeolitic Chemistry of Silver

Nam Ho Heo<sup>1,\*</sup>, Yang Kim<sup>2</sup>, Jong Jin Kim<sup>3</sup>, and Karl Seff<sup>4</sup>

<sup>1</sup>Laboratory of Structural Chemistry, Department of Applied Chemical Engineering, Kyungpook National University, Daegu 41566, Korea

<sup>2</sup>Department of Chemistry, College of Natural Science, Busan National University, Busan 46241, Korea

<sup>3</sup>Department of Earth System Science, College of Natural Science, YonSei University, Seoul 03722, Korea

<sup>4</sup>Department of Chemistry, University of Hawaii, 2545 The Mall, Honolulu, Hawaii 96822, U. S. A

### 1 Introduction

The void space of a zeolite is a medium, like space or a solvent, in which a chemistry can occur. Unlike those media, however, because a zeolite is a crystalline solid, the detailed structure of the product of a reaction or process can be observed crystallographically to relatively high precision. Accordingly, crystallography, especially single crystal crystallography, is a powerful method for the study of intrazeolitic chemistry.

$\text{Ag}^+$  has a particular affinity for zeolites, it exchanges easily and quantitatively into them from aqueous solution, usually replacing  $\text{Na}^+$  ions. For a variety of reasons including uptake of anions, incomplete exchange, and cation hydrolysis (which can lead to partial  $\text{H}^+$  exchange and, in turn, crystal damage), this cannot be said of most cations.  $\text{Ag}^+$  has none of these problems.

### 2 Experiment

To do an experiment in zeolite chemistry, the first step is usually to replace the exchangeable cations, usually  $\text{Na}^+$ , in the zeolite as it was synthesized with other cations, whichever ones one wants to study. That is generally done from aqueous solution. The second step (unless the objective is just to study the hydrated zeolite) is to dehydrate the zeolite to get the water out of the way. It is generally the dehydrated zeolite that has utility in catalysis and sorption. Also, other molecules of interest can be sorbed into an empty zeolite and those sorption structures can be learned. If those other molecules react, the reaction products can be seen. More complex steps of ion exchange, dehydration, and the sorption of more substances, all for various times and at various temperatures, may be used.

### 3 Results and Discussion

New small molecules and cations have been synthesized within silver containing zeolites, and their structures were determined using single crystal crystallography. Some of them are the hydronitrogens  $\text{N}_3\text{H}_5$  and  $\text{cyclo-N}_3\text{H}_3$ [1], octahedral  $\text{Ag}_6$ [2], and the silver halide clusters  $\text{Ag}_4\text{Cl}_4$ [3],  $\text{Ag}_4\text{Br}_4$ [4], and  $\text{Ag}_4\text{I}_4$ [5]. The silver halide clusters within their zeolites are ordered three-dimensional arrangements of identical quantum dots. The  $(\text{C}_3\text{O}_3\text{H}_3)_2^{2+}$  cation, a reduced dimer of  $\text{C}_3\text{O}_3\text{H}_3^{3+}$  (tripyrilium) is seen[3]; tripyrylium is planar and isoelectronic with benzene. The two rings bond together facially via their  $\pi^*$  orbitals in an eclipsed manner with a very short interplanar distance, 2.43 Å. Several examples

of silver containing zeolites are presented to Fig. 1, 2, and 3.

Molecules formed within a zeolite may be stable only within the zeolite; it may not be possible to isolate them. While such isolation should be possible for only  $\text{N}_3\text{H}_5$  and perhaps  $\text{cyclo-N}_3\text{H}_3$ , we do not easily foresee this to be the case for the other species.

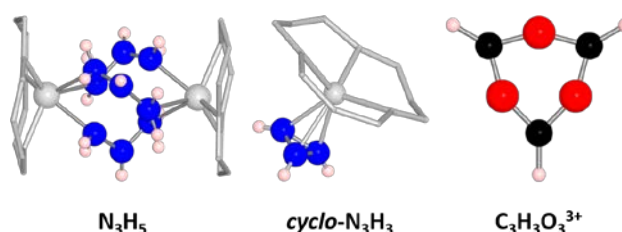


Fig. 1:  $\text{N}_3\text{H}_5$ ,  $\text{cyclo-N}_3\text{H}_3$ , and  $\text{C}_3\text{O}_3\text{H}_3^{3+}$

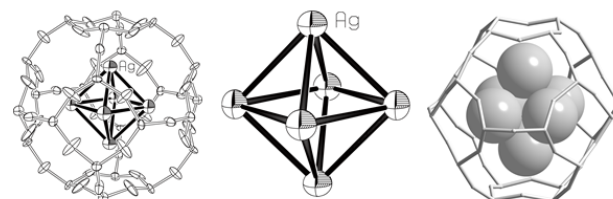


Fig. 2: Hexasilver molecule,  $\text{Ag}_6^0$ , in a sodalite cavity

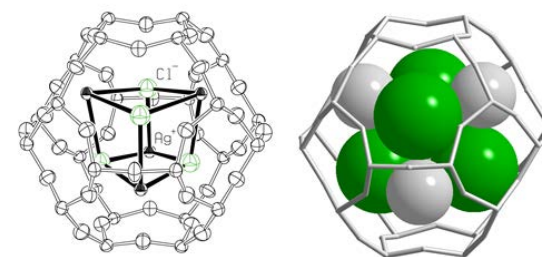


Fig. 3:  $\text{Ag}_4\text{Cl}_4$  cluster in a sodalite cavity

### References

- [1] Y. Kim. *et al.*, *J. Am. Chem. Soc* **99**, 7057 (1977).
- [2] Y. Kim *et al.*, *J. Am. Chem. Soc* **99**, 7055 (1977).
- [3] S. H. Kim. *et al.*, *J. Phys. Chem. C* **112**, 11181 (2008).
- [4] W. T. Lim. *et al.*, *Bull. Korean Chem. Soc* **26**, 1090 (2005).
- [5] N. H. Heo. *et al.*, *J. Phys. Chem. B* **108**, 3168 (2004).

\* nhheo@knu.ac.kr