The Intrazeolitic Chemistry of Silver

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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.

Ag⁺ has a particular affinity for zeolites, it exchanges easily and quantitatively into them from aqueous solution, usually replacing Na⁺ ions. For a variety of reasons including uptake of anions, incomplete exchange, and cation hydrolysis (which can lead to partial H⁺ exchange and, in turn, crystal damage), this cannot be said of most cations. 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 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 N₃H₅ and cyclo-N₃H₃[1], octahedral Ag₆[2], and the silver halide clusters Ag₄Cl₄[3], Ag₄Br₄[4], and Ag₄I₄[5]. The silver halide clusters within their zeolites are ordered three-dimensional arrangements of identical quantum dots. The (C₃O₃H₃)₂⁺ cation, a reduced dimer of C₃O₃H₃₃⁺ (tripyrylium) is seen[3]; tripyrylium is planar and iso electronic with benzene. The two rings bond together facially via their π* 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.

Fig. 1: N₃H₅, cyclo-N₃H₃, and C₃O₃H₃³⁺

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 N₃H₅ and perhaps cyclo-N₃H₃, we do not easily foresee this to be the case for the other species.

References

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