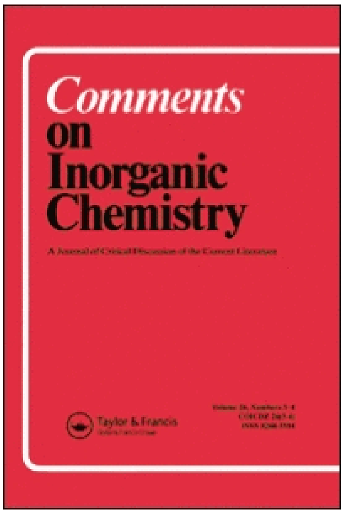

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DOING CHEMISTRY IN A ONE-NANOMETER TEST TUBE (IN A ZEOLITE)

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Zeolites have catalytic, ion-exchange, and sorption properties that make them valuable for a wide range of applications, from the cracking of crude oil to the drying of gases and liquids. Behind this great utility lies a fascinating chemistry that is too often summarized ("acid catalyst" or "desiccant") as though there were nothing more to be said. Well, there is a lot more to be said. There is plenty of new chemistry waiting to be learned from the study of zeolites.

This article is about doing real chemistry in zeolite cavities. It is not about the optimization of zeolites by trial-and-error methods for particular applications. And it involves "test tubes" that have a wide range of compositions, including those from soft glass to quartz.

In a 1-nm vessel, the walls are important. The chemistry that occurs in zeolites is therefore like surface chemistry, which makes it an extreme chemistry; this is the basis of the wide-ranging utility that zeolites enjoy. Furthermore, this remarkable "surface," because it is three-dimensional, can be seen with crystallographic precision. So can the products of a reaction or process, which can be identified and counted within the zeolite's channels and cavities.

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In fully dehydrated zeolites, the exchangeable cations coordinate to arrangements of oxide ions at the walls. This coordination, however, is usually woefully inadequate. The primary duty of the oxide ions of the zeolite framework is to satisfy the coordination requirements of the small framework cations such as Si^{4+} and Al^{3+}. This yields relatively inert and inflexible structures that are unable to simultaneously satisfy the coordination requirements of the exchangeable cations, which are far less demanding because their radii are larger and their charges smaller. To them, main-group and transition-metal cations, the dehydrated zeolite offers a short list of coordination situations on a take-it-or-leave-it basis, and each exchangeable cation must simply choose the best one available. (This is very much unlike the situation in solution where a cation can select its coordination geometry, its distance to each ligand atom, sometimes even its ligands, or reject the available ligands altogether by not dissolving.) These exchangeable cations (they may have evolved by further treatment to be H^+ or complex cationic clusters), by their inadequate coordination, chemical nature, and physical arrangement, usually govern the resulting chemistry.

Good chemistry is done by good chemists. Issues of purity and stoichiometry are as important in zeolite science as they are in other areas of chemistry. For example, the net reaction that occurs when S(g) is sorbed onto fully dehydrated, fully Cd^{2+}-exchanged zeolite X ($Cd_{46}Si_{100}Al_{92}O_{384}$ per unit cell)[1] is

$$\begin{aligned}13S_8 &\rightarrow 4S_4^{4+}(\text{tetrahedra}) + 16n\text{-}S_4^{2+}(\text{chains})\\ &\quad + 24S^{2-}(\text{coordinated to } Cd^{2+}) \qquad (1)\end{aligned}$$

This is a startling result, and the simple sorption process that might have been assumed lacking further information,

$$S_8(s) \rightarrow S_8(\text{sorbed}) \text{ or } 8S(\text{sorbed}), \qquad (2)$$

would altogether miss the chemical reality. With a different net reaction, iodine also undergoes intrazeolitic disproportionation upon sorption into Cd-X.[2] In both cases, an element disproportionated electronically to give unusual cationic clusters, some of which were new to chemistry, and simple anions (S^{2-} and I^-) that coordinate to the previously coordinatively unsaturated Cd^{2+} ions. The latter coordination is the primary driving force for these reactions; these coordinatively unsaturated Cd^{2+} ions have extracted anions from elements, leaving cations behind as residue. In both cases, the reaction proceeded to completion, until one of the product sites became full.

When the dehydration of fully Ag^+-exchanged zeolite X was attempted under vacuum with the temperature increasing slowly to 673 K,[3] the net reaction was quite complex. It appeared to be

$$\begin{aligned}&Ag_{92}^{+}\text{–X(hydrated)} \rightarrow Ag_{38}^{+}(Ag_8^{4+})_4(\textit{cyclo}\text{-}Ag_4^{2+})_4\text{–X(dehydrated)}\\&\quad + 6Ag^0\text{(exited the structure)} + 7.5O_2\text{(exited the structure)}\end{aligned} \tag{3}$$

When this was repeated in zeolitically dry flowing oxygen gas, the decomposition of the Ag_2O component of the chemical formula was suppressed by mass action and the net reaction became far simpler,[3]

$$Ag_{92}^{+}\text{–X(hydrated)} \rightarrow Ag_{92}^{+}\text{–X(dehydrated)}, \tag{4}$$

the simple dehydration that might have been expected when reaction (3) was performed. Ag^+–Ag^+ bonding could then be clearly seen.[4]

When anhydrous Na_{92}–X ($Na_{92}Si_{100}Al_{92}O_{384}$) was exposed to Cs(g), the product was Cs_{128}–X ($Cs_{128}Si_{100}Al_{92}O_{384}$). Per unit cell, 92 Na(g) atoms left the zeolite. The mean positive formal charge of each cesium cation was $92/128 = 0.72+$, and the structure of the resulting three-dimensional cationic continuum, held together by 36 6 s bonding electrons per 128 cesium ions, could be seen.[5,6] When Rb(g) was used, the unit cell formula was Rb_{140}–X,[7] and a different cationic continuum, with more atoms because Rb is smaller than Cs, filled the zeolite's channels and cavities.

When zeolite A in its Na^+ form ($Na_{12}Si_{12}Al_{12}O_{48} \cdot 27H_2O$ per unit cell[8]) is exhaustively ion exchanged at 301 K with ultrapure $CsNO_3$(aq), the net reaction is

$$Na_{12}\text{-A} + 7Cs^+ \rightarrow Cs_7Na_5\text{-A} + 7Na^+,^{[9]} \tag{5}$$

which amounts to incomplete exchange. When this is done with CsOH, over-exchange occurs:

$$Na_{12}\text{-A} + 13Cs^+ + OH^- \rightarrow Cs_{13}(OH)\text{-A} + 12Na^+.^{[10]} \tag{6}$$

In both cases, the reason why the simple complete ion-exchange reaction

$$Na_{12}\text{-A} + 12Cs^+ \rightarrow Cs_{12}\text{-A} + 12Na^+ \tag{7}$$

did not occur could be easily seen in their structures.

As reactions (5) and (6) exemplify, the result of an ion-exchange experiment is infrequently as simple as it could be. There is underexchange (reaction 5) and, when some anions (usually hydroxide or halide) accompany cations into the zeolite, over-exchange (reaction 6). For cations that can hydrolyze, the outcome of an ion-exchange experiment is often heavily dependent on the pH of the solution with which the zeolite is in equilibrium. Some cations are stable in aqueous solution only at low pHs, and some zeolite frameworks decompose at those pHs. To date all reports of ion exchange have been from aqueous solution or from undried (wet) polar organic solvents.[11,12]

Note that exchangeable (extraframework) cations are required only if the zeolite framework is negative, as is the case for $AlSiO_4$ or, somewhat more generally, $Al_xSi_{2-x}O_4$, $0 < x \leq 1$. Therefore those of composition SiO_2 and $AlPO_4$, and there are many, have no exchangeable cations.

Arguments regarding window size are often incorrect. For an anhydrous (empty) zeolite, an organic molecule too large to pass through a window may indeed not be sorbed. In a wet zeolite, however, mechanisms of passage involving ring opening appear to operate,[13] and violations of window-size arguments are rampant, especially for monatomic ions, both cations and anions. The rules of chemistry, we will recall, involve thermodynamics and dynamics, and these do not always reduce to "window size." Cooperative mechanisms may open rings, and one ring opening per cavity during the course of an experiment may admit an ion or molecule to each. The oxygen atoms may be surprisingly mobile at elevated temperatures or in the presence of water, allowing the momentary creation of openings that are much larger than the rings depicted in static structure models.

The experimental techniques of zeolite science are simple, but they are often misperformed. Some good chemists who have ventured into zeolite science have been unaware of some of the following considerations, and this has led to wasted effort and many publications on materials not understood by their authors to be ill defined. First of all, that dehydrated zeolites are truly excellent desiccants must not be overlooked. If water cannot be tolerated in a procedure, the reagents used must be zeolitically dried *in situ*. The walls of a vacuum system are a source of water unless they have been baked out, and unbakeable dry boxes are therefore anathema. In addition, dehydration must be done cautiously to avoid reaction between the zeolite and relatively high concentrations of hot steam. Due to selectivity, cations present in trace concentrations may preferentially ion exchange into a zeolite. Similarly, molecules present in trace concentrations in a vapor will, if they are more polar, be selectively sorbed. Zeolite powders and pellets, unlike single crystals, are generally not pure; other phases are present. Attempts to do ion exchange using aqueous flow through a powder may result in a range of compositions as percolation selects preferred pathways.

In designing an experiment, there should be a physical reason why a desired product should remain in the zeolite structure, rather than exiting it as the excess silver atoms and $O_2(g)$ did in reaction (3). Cations have an obligation to remain within a zeolite whose framework is anionic, and even cationic and neutral ionic clusters have an electrostatic reason to do so. Molecules that might coordinate to those cations, e.g., H_2O, NH_3, or NO_2, have a chemical reason to remain in a zeolite. Interactions between molecules and oxygens of the zeolite framework may be strong enough to keep them within the zeolite,[14]especially if the crystal is in an atmosphere of that gas or vapor as its structure is being determined. However, neutral atoms, neutral clusters of atoms, and molecules may be more stable (have a lower free energy) in their own phase outside the zeolite. For example, the sorption of metal carbonyls followed by their decomposition within a zeolite to give metal clusters has produced neither stable nor stoichiometric materials. The same is true when complexes prepared by sorption at high pressures (loading) are returned to ambient pressures, unless the windows are blocked.[15]

My work has generally proceeded as follows: select a single zeolite crystal, perform ion exchange if desired to introduce a cation of interest, and then, all without exposure to the atmosphere, dehydrate the crystal by increasing its temperature slowly under dynamic vacuum, do the chemistry one step at a time *in situ* within the vacuum system, seal off the capillary containing the crystal with a small flame, and determine the structure of that crystal. "Do the chemistry" has usually meant exposure to a gas or vapor, e.g., Zn(g), Cs(g), S(g), Xe, H_2, NO, D_2O, C_3H_6, or C_6H_6, at a temperature and pressure to be selected. There may be no chemistry done, or there may be more than one step, and other imaginative sequences are possible. "Dehydrate the crystal" includes the obligation of keeping it from rehydrating, or more insidiously of keeping its contents from reacting with water, during subsequent steps. Adjacent sections of the vacuum system must also be baked out, including an in-series tube of zeolite beads that is allowed to cool before the crystal to protect it from itinerant water molecules. The result of an experiment is seen crystallographically with additional support from other observations. If the dehydration procedure is not followed correctly, the unwanted water molecules can often be seen and counted in the resulting crystal structure.

It has been important in this work to prepare crystals that are simple enough (stoichiometric enough) for their structures to be reliably determined. Toward that end, some time (days) are spent, perhaps wasted, during sample preparation with the hope of reaching some end point. Sorbed molecules should have a symmetry that the zeolite framework is likely to support. Otherwise, they need to be very small. This is because the space group symmetry used to solve a structure is almost universally that of the zeolite framework. It is infrequently carried forward by the exchangeable cations and sorbed molecules because of their fractional occupancy, and (for most molecules) lower symmetry and orientations of lower symmetry within the zeolite. As a result, many positions of fractional occupancies are usually found, and chemical reasoning must be employed to interpret the results. For this reason, zeolite crystallography is usually less definitive than regular crystallography, just as powder crystallography is generally not as good as single-crystal crystallography, and the crystallography of poorly crystallized materials like clays is poorer than that of nicely crystallized substances.

Originally zeolites were found in nature; about 40 framework types have been identified. About 140 more have been made synthetically and this number is steadily increasing at the rate of about seven per year.[16] Many of these 180 framework morphologies can have a wide range of compositions, and this provides many research opportunities.

Chemical industry and national governments have supported zeolite research for the whole of its existence in pursuit of applications of great economic importance. Too often, a gold-rush mentality has prevailed. This will continue, but it would be good if more of us approached the field more systematically, more scientifically, because that is the better way to build a science. The science that underlies gold rushes is geology. For zeolites, it is chemistry.

REFERENCES

1. Song, M. K., Y. Kim, and K. Seff, 2003. Disproportionation of an element in a zeolite. I. Crystal structure of a sulfur sorption complex of dehydrated fully Cd^{2+}-exchanged zeolite X. Synthesis of tetrahedral S_4^{4+} and n-S_4^{2+}, two new polyatomic cations of sulfur. *J. Phys. Chem. B*, **107**, 3117–3123.

2. Song, M. K., E. Y. Choi, Y. Kim, and K. Seff, 2003. Disproportionation of an element in a zeolite. II. Crystal structure of an iodine sorption complex of dehydrated fully Cd^{2+}-exchanged zeolite X containing *n*-I_5^- as I^--I_3^+-I^- and square *cyclo*-I_4^{2+}. *J. Phys. Chem. B*, **107**, 10709–10714.
3. Kim, S. Y., Y. Kim, and K. Seff, 2003. Two crystal structures of fully dehydrated fully Ag^+-exchanged zeolite X. Dehydration in oxygen prevents Ag^+ reduction. Without oxygen, Ag_8^{n+} (T_d) and *cyclo*-Ag_4^{m+} (near S_4) form. *J. Phys. Chem. B*, **107**, 6938–6945. Errata: *ibid.* 10320.
4. Jansen, M. 1987. Homoatomic d10–d10 interactions: Their effects on structure and chemical and physical properties. *Angew. Chem. Int. Ed. Engl.*, **26**, 1098–1110.
5. Sun, T., K. Seff, N. H. Heo, and V. P. Petranovskii, 1993. A cationic cesium continuum in zeolite X. *Science*, **259**, 495–497.
6. Sun, T., K. Seff, N. H. Heo, and V. P. Petranovskii, 1994. A cationic cesium continuum in zeolite X. *J. Phys. Chem.*, **98**, 10156–10159.
7. Lee, S. H., Y. Kim, and K. Seff, 2000. A cationic rubidium continuum in zeolite X. *J. Phys. Chem. B*, **104**, 11162–11167.
8. Breck, D. W. 1974. *Zeolite Molecular Sieves*. Wiley, New York, 86.
9. Vance, T. B. Jr. and K. Seff, 1975. Hydrated and dehydrated crystal structures of seven-twelfths cesium-exchanged zeolite A. *J. Phys. Chem.*, **79**, 2163–2167.
10. Dejsupa, C., N. H. Heo, and K. Seff, 1989. Crystal structure of cesium zeolite A prepared by complete aqueous exchange. *Zeolites*, **9**, 146–151.
11. Ho, K., H. S. Lee, B. C. Leano, T. Sun, and K. Seff, 1995. Failure of ion exchange into zeolites A and X from four diverse non-aqueous solvents. *Zeolites*, **15**, 377–381.
12. Bae, D. and K. Seff, 1996. Co(II) exchange into zeolites A and X from formamide solution depends upon water content. *Zeolites*, **17**, 444–446.
13. Ryu, K. S., M. N. Bae, Y. Kim, and K. Seff, 2004. Further crystallographic confirmation that Cs^+ ions can occupy sodalite cavities and double six-rings. Crystal structure of fully dehydrated partially Cs^+-exchanged zeolite X. *Microporous Mesoporous Mater.*, **71**, 65–75.
14. Seff, K. and D. P. Shoemaker, 1967. The structures of zeolite sorption complexes. I. The structures of dehydrated zeolite 5A and its iodine sorption complex. *Acta Crystallogr.*, **22**, 162–170.
15. Heo, N. H., W. T. Lim, B. J. Kim, S. Y. Lee, M. C. Kim, and K. Seff, 1999. Crystal structures of encapsulates within zeolites. 3. Xenon in zeolite A. *J. Phys. Chem. B*, **103**, 1881–1889.
16. Baerlocher, Ch., L. B. McCusker, and D. H. Olson, 2007. *Atlas of Zeolite Framework Types*. Elsevier, Amsterdam, 1.