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Toward Inorganic Electrides

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Electrides are strongly reducing materials in which alkali metals (Li through Cs) ionize to form bound alkali cations and "excess" electrons.[1] The electrons reside in large cavities or channels or both in the host lattice. We report here the first synthesis of thermally stable inorganic electrides with cation-to-electron ratios of 1:1 as in organic electrides. Two pure silica zeolites, ITQ-4[2,3] and ITQ-7,[4] with pore diameters of ~7 Å,[4] absorb up to 40 wt % cesium from the vapor phase (even at room temperature). The optical and magnetic properties suggest ionization to form Cs^+ and e^- with substantial electron spin pairing. Although alkali metal adducts to *alumino*-silicate zeolites are well-known,[5] the cation-to-electron ratio is generally 3:1 or greater because these zeolites contain alkali cations prior to incorporation of the alkali metal.

Organic electrides are crystalline ionic compounds formed by reaction of alkali metals with organic complexants for the cations.[1,6] Alkali cations are strongly sequestered within cages formed from one or two of the complexant molecules. The electrons released by ionization of the alkali metal are trapped in the cavities and channels that exist between the complexed cations. Since organic electrides are thermally unstable and must be kept at temperatures below −40 °C, we sought to prepare *inorganic* electrides that are stable at and above room temperature. To have only one cation per electron, our attention was focused on nonionic pure silica zeolites with low concentrations of defects.

The addition of alkali metals to alumino-silicate zeolites that contain alkali cations to balance the negative charge introduced by aluminum has been extensively studied.[5,7] The excess electrons from the added alkali metals have been described as "solvated electrons",[8] and these materials have even been called "electrides".[5,9] Their structures and properties strongly support the notion that ionization of the alkali metal occurs and that the released electrons are shared by clusters of cations to form species such as $(M_n)^{(n-1)+}$, in which $n = 3, 4, 5, ...$ Added alkali metals can produce complex optical and magnetic behavior, such as antiferromagnetism,[10] ferro- or ferrimagnetism,[11] alkali-metal chain formation,[12] and the formation of alkali-metal anions (Na^-, K^-, or Rb^-).[13,14] Such complex behavior is not yet fully understood.

The zeolites used in this work, ITQ-4[2,3] and ITQ-7[4], have unit cells with formulas $Si_{32}0_{64}$ and $Si_{64}0_{128}$, respectively, and are free of preexisting cations. Both have rather open channels of diameter ~7 Å. As shown in Figure 1, ITQ-4 has separated sinusoidal channels in one direction, while ITQ-7 forms a 3D network of interconnected channels. These views show the shapes of the void spaces[6,15] as determined from the crystal structures.[2,4] The ^{29}Si NMR spectra show that they have less than 0.4 Si−O defects per 32 Si atoms. Powders are polycrystalline with linear dimensions from 0.1 to 20 μm.

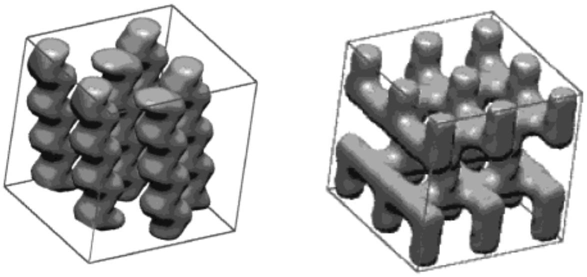

Figure 1. Perspective views of the channels in ITQ-4 (left) and ITQ-7 (right). The surfaces represent the loci of points that lie 0.75 Å from the van der Waals surfaces of the atoms.

To prepare silica-based electrides, the dehydrated zeolite and a weighed amount of cesium metal are sealed under vacuum in a borosilicate flask, and the cesium is heated to form a thin mirror on the walls of the vessel. The surface of the powdered zeolite sample turns blue within a few hours, even at room temperature. With frequent agitation the cesium is completely absorbed in a few days (ITQ-7) or weeks (ITQ-4). Heating at 50−60 °C overnight also completes the absorption. The samples have overall uniform Cs concentrations (typically within 10%) between and within crystals as indicated by energy dispersive spectroscopy. An important check on the net Cs^0 concentration is the measurement of the amount of H_2 produced by reaction of the evacuated product with water. Comparison with the *total* amount of base formed confirmed the low defect concentration, since SiOH groups would react with cesium to produce basic but nonreducing sites.

The strongest evidence for ionization to yield Cs^+ and trapped electrons comes from Kubelka−Munk analysis[16,17] of the reflectance spectra. As shown in Figure 2, dilute Cs samples have only a broad near-IR peak centered at 1400 nm that is remarkably similar to those of solvated electrons in ammonia[18] and of electrides with localized electrons.[19] Increasing the cesium content produces a shoulder or peak at 830 nm and a rising absorbance at the blue end of the spectrum. Since there is no evidence of a peak, even down to 240 nm, this continued rise in absorbance at short wavelengths might be due to a shift of the silica absorption toward the visible at high cesium concentrations. The color changes from blue-gray to tan upon "annealing" at ~100 °C, but the only change in spectral shape is a decrease of the relative magnitude of the 830 nm shoulder or peak. The yield of hydrogen upon addition of water is unchanged from that of fresh samples.

As shown in Figure 3, the X-ray powder diffraction pattern of ITQ-4 displays an increasing amorphous character as the concentration of cesium increases. Remarkably, however, treatment with

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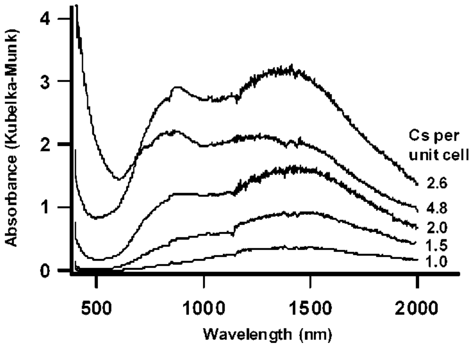

Figure 2. Absorbance obtained by Kubelka−Munk[16,17] analysis of the reflectance spectra for various loadings of Cs in ITQ-4.

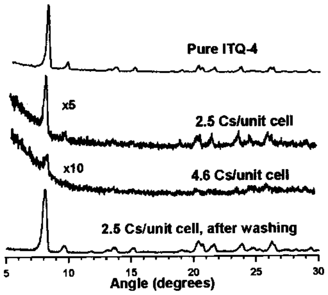

Figure 3. Powder X-ray diffraction patterns of ITQ-4 with and without cesium.

water and subsequent neutralization and washing restores the X-ray pattern. Evidently, incorporation of cesium produces a reversible distortion of the silica lattice. Scanning electron microscope images of air-oxidized crystallites show that there is no change in crystal morphology up to 4 Cs per 32 Si.

Additional evidence for delocalization of the electron following ionization of Cs comes from ^{29}Si and ^{133}Cs NMR spectra, obtained over wide scan regions. Even at Cs concentrations as low as 1 Cs per unit cell, both disappear into the baseline. By contrast, alkali metals in alumino-silicate zeolites often show alkali-metal, silicon and aluminum NMR spectra, even at high loadings.[10,13] Evidently, in our case the electron density is spread out enough to broaden the NMR lines substantially. The predominant overall diamagnetism (see below) is not in conflict with paramagnetic broadening of the ^{29}Si and ^{133}Cs NMR spectra. Rapid exchange between paired and unpaired electrons would lead to such broadening, provided the electron density overlaps sufficiently with the nuclei. Air oxidation restores the NMR spectra.

As with metal−ammonia solutions[18] and electrides that have large open channels between trapping sites,[19] electron-spin pairing in cesium-doped ITQ-4 and ITQ-7 is extensive. Magnetic susceptibilities and EPR spectra show only a minor “Curie Tail”, corresponding to paramagnetism from less than 1% of the total cesium. It should be noted that the metal concentrations are in the range of 0.5−2 M. (The electrons in metal−ammonia solutions are predominantly spin-paired at such concentrations.) The magnetic behavior is difficult to interpret in detail because even the undoped zeolites have low concentrations of paramagnetic species.

These materials are powerful reducing agents. In addition to their quantitative formation of hydrogen by reduction of water, the included cesium can reduce aromatic molecules to radical anions. Even benzene, which is difficult to reduce in solution, forms the benzene radical anion within the pores of the zeolite, as shown by both EPR and optical spectra.

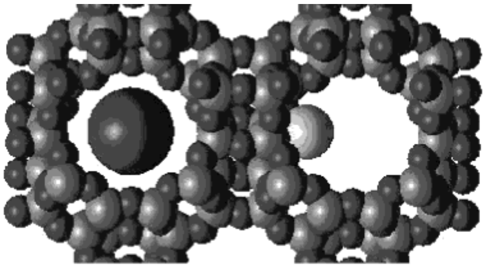

Figure 4. Space-filling representation of Cs^0 (dark sphere) and Cs^+ (light sphere) in the channels of ITQ-4. Dark atoms are oxygen; lighter atoms are silicon.

Possible cesium-containing candidates within the pores are Cs^+, Cs^0, Cs_2^+, Cs_2 and chains of Cs atoms or ions. The most likely scenario is ionization to form Cs^+ and itinerent electrons. As shown in Figure 4, within a channel there are many sites at which Cs^+ can be bound by three or more Si−O−Si units, whereas the large neutral cesium atom would be only weakly bound. Interactions of Cs^+ ions with the silica lattice could introduce reversible disorder. The released electron could then occupy the remaining free space, with a tendency for the strong antiferromagnetic coupling that is characteristic of concentrated trapped electrons. With increasing cesium concentration the amount of free space per electron would decrease, which could be responsible for the dramatic changes in the optical spectra.

In addition to the results described here, we have added Na, K, and Rb to ITQ-4 and cesium to two other silica zeolites. An ideal candidate for a *stoichiometric* inorganic electride would be a pure silica zeolite with specific cation-trapping sites and an equal number of large cavities or channels in which the released electrons could be trapped.

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