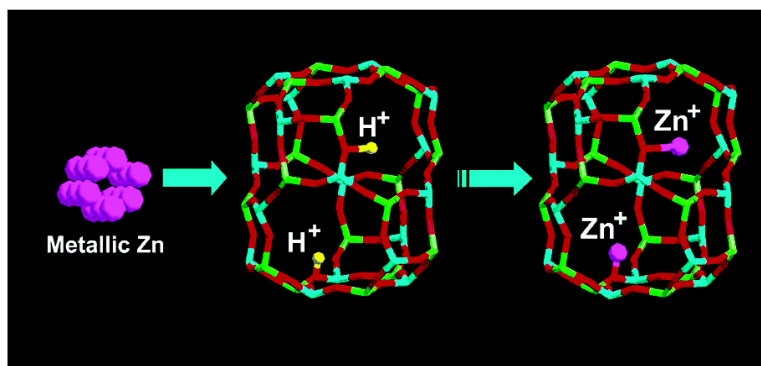


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Chemical Formation of Mononuclear Univalent Zinc in a Microporous Crystalline Silicoaluminophosphate

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When it forms compounds with oxidizing agents, metallic zinc easily loses its two valence electrons to become the Zn^{2+} cation. The formation of univalent Zn^+ is difficult through a chemical method under normal conditions. Although the presence of univalent zinc in the system containing metallic Zn and fused $ZnCl_2$ has been evidenced by Raman spectroscopy, the univalent species exist as diamagnetic $(Zn-Zn)^{2+}$ pairs,¹ and no further magnetic properties can be observed for this ion pair. To our knowledge, mononuclear univalent zinc, which contains unpaired electrons and should exhibit paramagnetic properties, was produced only through physical methods such as electron (ion)-impact ionization,² glow discharge,³ and γ -irradiation,⁴ and most of the produced mononuclear Zn^+ species existed in a gas phase without their magnetic properties elucidated. The chemical preparation of compounds containing mononuclear univalent zinc has not been successful yet. Nevertheless, if there is a microspace with an oxidizing site that can accept only one electron, a Zn atom may react with this site to form a mononuclear Zn^+ cation. Of course, the prerequisite is that the driving force for the formed Zn^+ cations to get paired is smaller than the force for the cations to dissociate from the particular sites. The most suitable materials to offer such microspaces are molecular sieves such as zeolites and aluminophosphate-based compounds that possess microcages and/or channels.⁵ In the microcages, isolated Brønsted acidic sites (OH groups bridging a Si and an Al atom) may be produced.⁶ In principle, each of these Brønsted acidic sites can react with one Zn atom to form one Zn^+ cation, reducing its own H^+ to H in the meantime. The formed H atoms combine to be released as H_2 .

To examine the effectiveness of this approach, we chose a silicoaluminophosphate with a chabazite (CHA) structure as the microspace provider to interact with metallic zinc. This molecular sieve (designated SAPO-CHA) has elongated cages interconnected through eight-membered T-ring (T stands for Al, P, or Si) windows in three directions. The diameter of the window is about 0.43 nm, large enough for a single Zn atom to penetrate inside the cages and to move from one cage to an adjacent one. Inside each cage, the longest $O\cdots O$ contact distance is about 0.9 nm, and the shortest one is about 0.7 nm. The free space for each cage allows more than one Zn atom to be accommodated inside. Moreover, because some of the P atoms are replaced by Si atoms in the framework of SAPO-CHA, negative charges are inevitably present, and to balance these negative charges, Brønsted acidic sites are introduced in the formation of detemplated SAPO-CHA. It has previously been revealed⁷ that four crystallographically independent framework O atoms are present in the structure of SAPO-CHA, and two of these framework O atoms (O1 and O2) are possibly associated with a proton. Accordingly, two types of Brønsted acidic sites are able to form in the micocages. However, because the occupancy of the protons of the Brønsted acidic sites is much less than 1, not all of

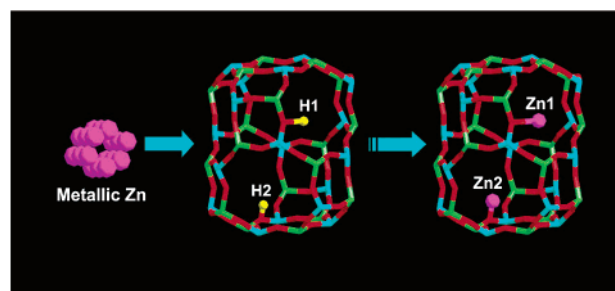


Figure 1. Schematic representation of the formation of two Zn cations in one CHA cage of SAPO-CHA through the reaction of metallic zinc with protons of two respective Brønsted acidic sites. Light blue, P or Si; green, Al; red, O; yellow, H; purple, Zn.

the O1 and O2 atoms in the chabazite cages of SAPO-CHA are bound to a proton.

On the basis of inductively coupled plasma (ICP) analysis, the molar composition for the detemplated SAPO-CHA sample we obtained from a hydrothermal reaction system was $H_{0.25}(AlP_{0.75}Si_{0.25})O_4$. It is inferred that for each chabazite cage of the SAPO-CHA material we synthesized, there are about 1.5 Brønsted acidic sites on average. Practically, this implies that of every two cages, one has a single Brønsted acidic site, whereas the other has two such sites. We evacuated the detemplated SAPO-CHA sample at about 450 °C, and the evacuated sample was sealed with metallic zinc in a Pyrex glass tube. The tube was heated at about 450 °C so that the metallic zinc vaporizes to react with the protons in the SAPO-CHA material. Following this treatment for about 40 h, the Pyrex glass tube was cooled slowly to room temperature. To remove physically adsorbed Zn atoms from the cages of SAPO-CHA, the end of the tube with metallic zinc was cooled before the end with the SAPO-CHA sample. The final product after this chemical vapor reaction is designated Zn@SAPO-CHA.

ICP analysis indicated that the molar composition of Zn@SAPO-CHA was very close to $Zn_{0.25}(AlP_{0.75}Si_{0.25})O_4$. This composition suggests that the Zn atoms have replaced all of the protons in the detemplated SAPO-CHA through the chemical vapor reaction. Figure 1 schematically shows the process of the chemical reaction of zinc metal with two Brønsted acidic sites in the CHA cage of SAPO-CHA. Some of the CHA cages each contain only one Brønsted acidic site so that a single zinc cation should be formed in each of these cages. Because one Zn replaces one H^+ in the SAPO-CHA cage, it is possible that the formed zinc cation exists as Zn^+ . If the formed Zn^+ ions remain mononuclear, paramagnetic properties arise.

To prove the existence of mononuclear Zn^+ species, electron spin resonance (ESR) spectroscopy and magnetic susceptibility measurements were performed for the Zn@SAPO-CHA under the protection of pure argon. Figure 2 illustrates the ESR spectrum of the Zn@SAPO-CHA material recorded on a Bruker ER 200D ESR

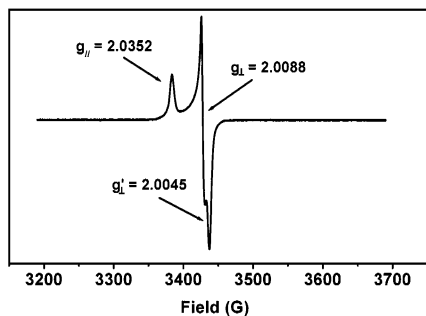


Figure 2. ESR spectrum for Zn@SAPO-CHA at room temperature.

spectrometer. It is clearly seen that strong ESR signals appear in the spectrum. For comparison, we also obtained the ESR spectra for the detemplated SAPO-CHA, the metallic zinc, and a ZnCl₂ prepared by reaction of the metallic zinc with hydrochloric acid. No ESR signal was observed for these samples, indicating that the ESR signals of the Zn@SAPO-CHA material are not due to the presence of magnetic impurities. Two possibilities arise to account for the strong ESR signals of Zn@SAPO-CHA. One is that mononuclear Zn²⁺ cations with unpaired 4s electrons exist in Zn@SAPO-CHA, and the other is that paramagnetic centers form in the framework of the microporous material. However, the reaction of metallic Zn with porous silica (silicalite-I), porous aluminophosphate (AlPO-CHA), and Na⁺-exchanged SAPO-CHA, all of which lack Brønsted acidic sites, under similar reaction conditions does not lead to paramagnetic products. Furthermore, if the detemplated SAPO-CHA is treated with metallic Na similarly, the ESR spectrum of the treated sample is essentially the same as that of the parent SAPO-CHA. Obviously, the paramagnetic behavior of Zn@SAPO-CHA cannot be due to the zeolitic framework varied by the introduction of metallic Zn. The only possibility is the existence of Zn²⁺ cations formed from the reaction of Zn with the protons.

Figure 2 also indicates that the *g* factors of the ESR spectrum of the Zn@SAPO-CHA compound exhibit anisotropy⁸ because both *g*_⊥ and *g*_∥ values are given. Furthermore, there are two *g*_⊥ values corresponding to the two crystallographically independent Zn²⁺ cations that have replaced the protons of the two different Brønsted acidic sites. The *g*_∥ value is 2.0352, but no splitting is discernible, probably because the *g* factors for the two different types of Zn²⁺ cations are identical or very close in the parallel direction. Anisotropy of *g*-factors due to uniaxial symmetry is not unusual for paramagnetic species occluded in the cages of other zeolites.⁹

The magnetic susceptibilities of the Zn@SAPO-CHA, the detemplated SAPO-CHA, and the metallic zinc were measured over the temperature range 2–300 K on a Quantum Design MPMS-5T magnetic property measurement system. Both detemplated SAPO-CHA and metallic Zn show diamagnetic susceptibility values, in agreement with the ESR results. The plot of the magnetic susceptibilities in emu per gram of sample, after subtraction of the corresponding diamagnetic values of the detemplated SAPO-CHA and metallic zinc, for Zn@SAPO-CHA against temperature is displayed in Figure 3. An obvious antiferromagnetic behavior at low temperatures is seen from the temperature dependence of the susceptibility with the Néel point being at about 4 K. The

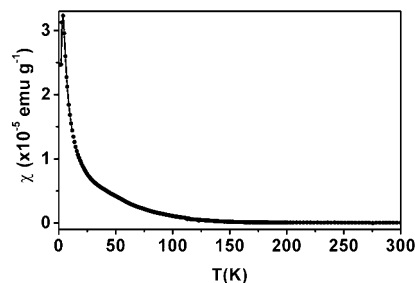


Figure 3. Temperature dependence of mass magnetic susceptibility of Zn@SAPO-CHA.

antiferromagnetism indicates that, although the Zn²⁺ ions are separated by the cages and/or cage walls in Zn@SAPO-CHA, the magnetic moments of these ions interact with each other, and magnetic ordering occurs. Antiferromagnetic interactions have often been observed¹⁰ for magnetic centers in the framework positions of a zeolite-like open-framework compound.

Although zeolites have previously been used to prepare paramagnetic clusters such as Na₄³⁺ and K₄³⁺,¹¹ no protons as an oxidizing agent are involved in the formation of these clusters. Formation of mononuclear univalent zinc through chemical reaction with protons represents a new approach that opens vast vistas for the preparation of interesting paramagnetic compounds with univalent metal species.

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Supporting Information Available: Preparation procedures for SAPO-CHA and Zn@SAPO-CHA, and figures of the XRD patterns, ESR spectra, and the experimental details for the measurements (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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