structure only shows one monocation that is valence localized. Mössbauer spectra were collected in the range of 300–120 K for a microcrystalline sample of the I_3^- salt of **1** prepared from CH_2Cl_2 as was the crystal employed in the structure determination. No quadrupole-split doublet ($\Delta E_Q \simeq 1.85$ mm/s) that could be assigned to a Mössbauer-delocalized complex could be seen; only one Fe(III) doublet and one Fe(II) doublet could be seen. In the previous work,[6] the I_3^- salt of the mixed-valence monocation **1** was prepared from benzene with an *excess* of I_2, not from CH_2Cl_2 with a stoichiometric amount of I_2. Additional work that will be described in a later paper suggests that the valence-delocalized Mössbauer doublet reported[6] before comes from the I_3^- salt of the carbenium cation form of **1** that inadvertently precipitates from benzene.

Acknowledgment. We are grateful for funding from the National Institutes of Health (Grant HL13652).

Supplementary Material Available: Tables of positional parameters, thermal parameters, and structure factors (14 pages). Ordering information is given on any current masthead page.

School of Chemical Sciences
University of Illinois
Urbana, Illinois 61801

Michael F. Moore
Scott R. Wilson
David N. Hendrickson*

Department of Chemistry
University of Connecticut
Storrs, Connecticut 06268

Ulrich T. Mueller-Westerhoff

Received April 2, 1984

The Framework Chemistry of Zeolites: ^{27}Al MASNMR of Extralattice Tetrahedral Aluminum Species

Sir:

The chemical, physical, and catalytic properties of zeolites are greatly influenced by their framework and nonframework composition. The aluminum content of the zeolite framework can be modified by chemical and/or thermal treatments. Numerous procedures have been developed. Chemical treatments of zeolites with $SiCl_4$,[1] for example, result in high-silica forms. Perhaps the most widely used technique is hydrothermal treatment.[2] These procedures are believed to increase the framework Si/Al ratio by effecting a migration of framework aluminum into nonlattice positions and in some cases from the zeolite. The exact nature of the extralattice aluminum species, the mechanism of this dealumination, the remaining framework defect structure, and the mechanism by which it is cured are not known. We present here the results of a study in which the formation of a nonframework tetrahedral aluminum species upon dealumination by thermal treatment of ion-exchanged zeolite A is followed by ^{29}Si and ^{27}Al MASNMR.

Pluth and Smith have reported finding electron density in the center of the sodalite unit in the determination of the crystal structures of dehydrated Ca^{2+}- and Sr^{2+}-exchanged zeolite A.[3,4] They have assumed this to be partial occupancy by disordered AlO_4* species. This electron density has been observed for Ca–X as well as most samples of zeolite A exchanged with divalent cations, but not the monovalent-exchanged samples.[4,5] Although Basler and Maiwald[6] have found ^{1}H NMR evidence for an aluminum species occluded during synthesis in the sodalite unit of zeolite Na–A dried at 90 °C, the absence of AlO_4* in their structural solution of monovalent-exchanged zeolite A led Pluth and Smith to suggest that the aluminate species develops during ion exchange with divalent ions or during the subsequent dehydration.

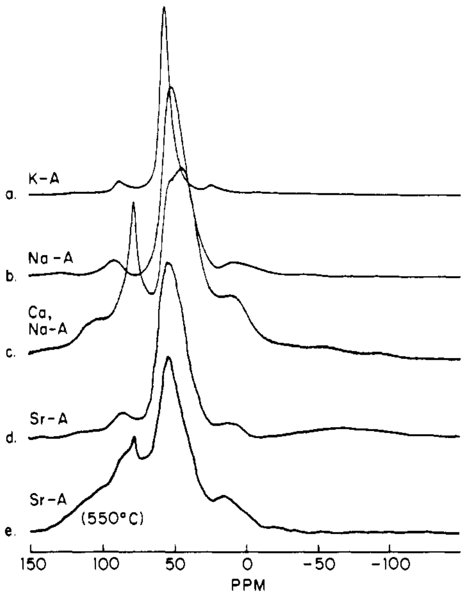

Figure 1. ^{27}Al MASNMR spectra of K–A, Na–A, Ca,Na–A, Sr–A, and Sr–A (550 °C).

We have also previously reported evidence from neutron powder diffraction studies for a 4-coordinate aluminum species in the center of the sodalite unit in H–Y zeolites treated with steam/NH_3 and $SiCl_4$.[7]

High-resolution magic angle spinning NMR (MASNMR) has recently been shown to be a very useful tool for zeolite characterization[8] of both the framework composition and extralattice species. Silicon-29 MASNMR is particularly useful for studying the change in the silicon–aluminum ordering in the zeolite framework upon treatment.[9] Aluminum-27 MASNMR has been used in the differentiation of the tetrahedral aluminum sites from the extralattice sites generated on steaming[10] and $SiCl_4$ treatment.[11] For both cases, 6-coordinate extralattice aluminum has been observed. In the unwashed $SiCl_4$-treated zeolites, a tetrahedral $AlCl_4^-$ species has also been identified. More recently, Engelhardt et al.[12] have used ^{27}Al MASNMR to study room-temperature dried

---

(1) Beyer, H. K.; Belenykaja, I. In "Catalysis by Zeolites"; Imelik, B., et al., Eds.; Elsevier: Amsterdam, 1980; pp 203–210.

(2) Scherzer, J. *J. Catal.* **1978**, *54*, 285 and references therein.

(3) Pluth, J. J.; Smith, J. V. *J. Am. Chem. Soc.* **1983**, *105*, 1192.

(4) Pluth, J. J.; Smith, J. V. *J. Am. Chem. Soc.* **1982**, *104*, 6977.

(5) Although the density for the corresponding oxygen atoms for a vacuum-dehydrated silver hydrogen zeolite A was not found, electron density at the center of the sodalite unit was reported and assigned as aluminum (Gellens, L. R.; Smith, J. V.; Pluth, J. J. *J. Am. Chem. Soc.* **1983**, *105*, 51).

(6) Basler, W. D.; Maiwald, W. *J. Phys. Chem.* **1979**, *83*, 2148. Basler, W. D.; Maiwald, W. In "Magnetic Resonance in Colloid and Interface Science"; Fraissaid, J. P., Resing, H. A., Eds.; Reidel: Boston, 1980; pp 437–442.

(7) Parise, J. B.; Corbin, D. R.; Abrams, L.; Cox, D. E. *Acta Crystallogr., Sect. C*, in press.

(8) Lippmaa, E.; Mägi, M.; Samoson, A.; Engelhardt, G.; Grimmer, A.-R. *J. Am. Chem. Soc.* **1980**, *102*, 4889. Melchior, M. T.; Vaughan, D. E. W.; Jarman, R. H.; Jacobson, A. J. *Nature (London)* **1982**, *298*, 455. Fyfe, C. A.; Thomas, J. M.; Klinowski, J.; Gobbi, G. C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 259–275.

(9) Vega, A. J. In "Intrazeolite Chemistry", Stucky, G. D., Dwyer, F. G., Eds.; American Chemical Society: Washington, D.C., 1983; pp 217–230.

(10) Maxwell, I. E.; von Erp, W. A.; Hays, G. R.; Couperus, T.; Huis, R.; Clague, A. D. H. *J. Chem. Soc., Chem. Commun.* **1982**, 523.

(11) Klinowski, J.; Thomas, J. M.; Fyfe, C. A.; Gobbi, G. C.; Hartman, J. S. *Inorg. Chem.* **1983**, *22*, 63.

(12) Engelhardt, G.; Fahlke, B.; Mägi, M.; Lippmaa, E. *Zeolites* **1983**, *3*, 292.

0020-1669/84/1323-2920$01.50/0

aluminosilicate intermediates in the synthesis of zeolite A. No signals due to tetrahedral aluminate or octahedral AlO_6 species were detected.

Samples of zeolite A, exchanged with various cations, were examined to determine if extralattice aluminum species could be detected by ^{27}Al NMR.[13] Commercial samples of K–A, Na–A, and Ca,Na–A (Linde 3A, 4A, 5A, respectively) zeolites were examined as received by ^{27}Al MASNMR (see Figure 1). For K–A and Na–A, only framework tetrahedral aluminum species are observed with chemical shifts 57 and 52 ppm, respectively. However, for the Ca,Na–A material, an intense, narrow resonance at 78 ppm is also observed.

Chemical shifts for ^{27}Al NMR spectra of a variety of tetrahedral aluminum-containing compounds are reported in the literature. For zeolites, the chemical shift for the framework tetrahedral aluminum whose nearest neighbors are silicon and/or aluminum is found in the range of 65–51 ppm as shown in Figure 1.[14] The ^{27}Al NMR spectrum of a solution of $Al(OH)_4^-$ exhibits a chemical shift of 80 ppm.[15] Chemical shifts for various solid aluminates fall in the range of 65–77 ppm.[16] The resonance observed at 78 ppm for the Ca^{2+}-exchanged zeolite A samples corresponds to that expected for a tetrahedral anion such as $Al(OH)_4^-$ or $(AlO_2^-\cdot 2H_2O)$. Similarly, for the sodalite of composition $Na_8[Al(OH)_4]_x[(H_2O)_5OH]_{2-x}[(Al_6Si_6)O_{24}]$, two resonances in the ^{27}Al MASNMR are observed at 80 and 56 ppm. The peak at 56 ppm corresponds to tetrahedral framework aluminum and the resonance at 80 ppm to extralattice $Al(OH)_4^-$ as verified from the single-crystal X-ray structural determination.[17] For Sr^{2+}-exchanged A,[18] a weak signal is also detected at 78 ppm as shown in Figure 1d.

The observation of the resonance at ca. 78 ppm in the ^{27}Al MASNMR spectra for the divalent cation-exchanged samples of zeolite A but not for monovalent-exchanged samples and its assignment to extraframework aluminum are thus in agreement with the structural results of Pluth and Smith. The intensity of the signal increased dramatically after calcination at 550 °C in flowing air (see Figure 1e). This increased displacement of aluminum from the framework on heating is also suggested by ^{29}Si MASNMR[19] results, which reflect an increase in the framework Si/Al ratio from 1.00 to 1.03 (±0.01).[20]

The spectrum of the tetrahedral framework aluminum in Ca,Na–A shown in Figure 1c is unusual because two peaks at 54 and 43 ppm are observed. The latter is well outside the range characteristic of framework aluminum, 65–51 ppm. This observation of the change in chemical shift for the ^{27}Al NMR, although unique, is analogous to the shift in the ^{29}Si NMR of partially Li-exchanged zeolite A as reported by Melchior et al.[21] They found the ^{29}Si chemical shift changes about 4 ppm between Na–A and fully exchanged Li–A. We have assigned the peak at 43 ppm to a chemical shift for Al near hydrated Ca^{2+}. The intensity is consistent with the cation content of 5A (i.e., Ca_4Na_4–A). We have examined the effect of hydration and degree of Ca^{2+} exchange[22] on the spectrum. As the water content decreases, the intensities of the peaks at 43 and 78 ppm decrease. The loss of intensity of the peaks probably results from the dehydroxylation of the $Ca(OH_2)_x^{2+}$ and $Al(OH)_4^-$ species. Diffuse-reflectance infrared spectra in the hydroxyl region of partially dehydrated samples of Ca,Na–A are in agreement with the literature for Ca–OH species in other calcium-containing zeolites.[23] The disappearance of the 43 ppm peak is not due to a gradual broadening of the peak as has been observed in ZSM-5.[24] The latter results indicate a gradual increase of the quadrupolar broadening, while in our case the change is abrupt. For a series of samples in which the calcium content increases and the dehydration temperature is held constant (see Figure 2), the intensities of the peaks at 43 and 78 ppm increase.

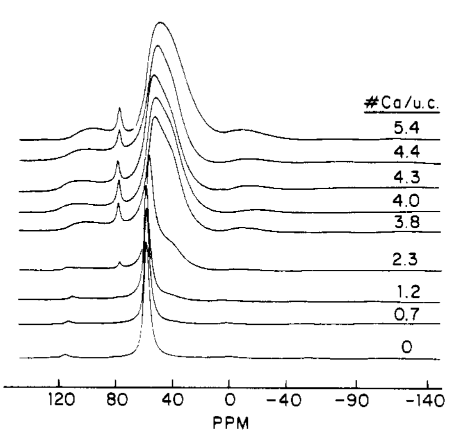

Figure 2. Effect of degree of Ca^{2+} exchange on the ^{27}Al MASNMR spectra of zeolite A.

In their structure solution, Pluth and Smith[3] locate the Ca^{2+} ion near the center of the 6-rings. Four-fifths of the calcium ions project into the supercage and one-fifth into the sodalite unit. Neutron diffraction results[25] for 5A (Ca/Na = 5/2) also have been interpreted in terms of both Ca and Na being associated with the 6-rings of the β cage. Severe distortion of the 6-ring is observed due to Ca atom coordination to the ring. With up to $x = 4$ in $Na_{12-x}Ca_xA$, the electrostatic energy can be minimized by a tetrahedral arrangement of the Ca atoms in the eight 6-ring faces of the sodalite cages. With higher calcium content, dehydration results in a lowering of the local unit cell symmetry, Ca ion siting in adjacent 6-ring faces, and even greater weakening of the framework metal atom to oxygen bonds in these shared 6-rings. The strain induced on the lattice may be relieved by the displacement of framework

---

(13) Aluminum-27 MAS spectra are obtained at 78 MHz on a Bruker CXP-300 spectrometer. Several spectra are obtained at spinning rates of 2–5 KHz to identify the spinning sidebands. Typically, 1000 scans are averaged with use of 30° pulses and 0.1-s recycle time. Chemical shifts are referenced to external 1 M $Al(NO_3)_3$ (0 ppm) in H_2O.

(14) Fyfe, C. A.; et al. *J. Phys. Chem.* **1982**, *86*, 1247.

(15) O'Reilly, D. E. *J. Chem. Phys.* **1960**, *32*, 1007.

(16) Müller, D.; Gessner, W.; Behrens, H.-J.; Scheller, G. *Chem. Phys. Lett.* **1981**, *79*, 59.

(17) Gier, T. E.; Chen, H. Y.; Vega, A. J.; Farlee, R. D.; Chase, D. B.; Corbin, D. R.; Stucky, G. D., manuscript in preparation.

(18) A sample of Na-A (40 g) was exchanged with 400 cm^3 of a 10% $Sr(NO_3)_2$ solution at 90 °C for 1 h. This procedure was repeated three times. After filtering and thorough washing with distilled water, the sample was dried at 110 °C.

(19) Silicon-29 MAS spectra was obtained at 60 MHz on a Bruker CXP-300 spectrometer, without proton cross-polarization or decoupling. The ^{29}Si spin–lattice relaxation times of representative samples are determined from inversion-recovery experiments, and conditions are then chosen to avoid saturation. Typically, ca. 7° pulses and 0.5-s recycle time is used to obtain quantitative spectra with accumulation times of 1–6 h. Chemical shifts are referenced to $(CH_3)_4Si$ with use of external hexamethylcyclotrisiloxane (−9.2 ppm) in $CHCl_3$ as the secondary standard.

(20) The calcination (550 °C) of a silver-exchanged zeolite A led to a similar increase in the framework Si/Al ratio as measured by the ^{29}Si MASNMR, indicating dealumination.[5]

(21) Melchior, M. T.; Vaughan, D. E. W.; Jacobson, A. J.; Pictroski, C. F. Sixth International Zeolite Conference, Reno, NV, July 1983; Abstract S-44.

(22) Samples of Linde 4A were ion exchanged with solutions of $Ca(NO_3)_2$. After thorough washing and drying at 110 °C, the samples were calcined at 300 °C for 10 h under flowing air. The zeolites were then placed over saturated NH_4Cl solution to rehydrate.

(23) Uytterhoeven, J. B.; Schoonheydt, R.; Liengme, B. V.; Hall, W. K. *J. Catal.* **1969**, *13*, 425. Costenoble, M. L.; Mortier, W. J.; Uytterhoeven, J. B. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 466. Kustov, L. M.; Borovkov, V. Y.; Kazansky, V. *B. J. Catal.* **1981**, *72*, 149. Jacobs, P. A.; Uytterhoeven, J. B. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 373.

(24) Such a broadening has been observed in dehydrated ZSM-5 zeolite: Kentgens, A. P. M.; Scholle, K. F. M. G. J.; Veeman, W. S. *J. Phys. Chem.* **1983**, *87*, 4357.

(25) Adams, J. M.; Haselden, D. A. *J. Solid State Chem.* **1984**, *51*, 83–90.

aluminum into some of the sodalite units. We consider the dehydration of $Ca(OH_2)_x^{2+}$ to $Ca(OH)^+$ and the stabilization of the anionic aluminum species to be important in the dealumination process as observed with divalent ions as opposed to monovalent cation-exchanged zeolite A. The terminal OH^- group is available for nucleophilic attack at the aluminum site to help initiate the dealumination reaction. Infrared and X-ray and neutron diffraction studies of these samples are presently being pursued to determine the role of the divalent species in the dealumination process.

Acknowledgment. Discussions with A. J. Vega, D. B. Chase, and L. Abrams are appreciated. The excellent technical assistance of R. F. Carver is acknowledged.

Registry No. $Al(OH)_4^-$, 14485-39-3; ^{29}Si, 14304-87-1; Al, 7429-90-5.

---

(26) Contribution No. 3468.

Central Research & Development Department[26]
Experimental Station
E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

D. R. Corbin*
R. D. Farlee
G. D. Stucky

Received April 2, 1984

An Improved Synthesis of TeF_5OF

Sir:

Recently, we reported[1] the synthesis and characterization of the previously unknown hypofluorite TeF_5OF, according to

$$\mathrm{CsTeF_5O + FOSO_2F \xrightarrow{-45\ ^\circ C} CsSO_3F + TeF_5OF}$$

This reaction represented a new synthetic route to hypofluorites, but it did entail drawbacks. Among these were the need for careful low-temperature control, long reaction times (9 days), the requirement for excess $CsTeF_5O$, and the less than optimal yields (~70%). Furthermore, the necessity to prepare and handle the treacherously explosive $FOSO_2F$[2,3] was a disadvantage.

We now report a new and improved process for the synthesis of TeF_5OF by means of the reaction

$$\mathrm{B(OTeF_5)_3 + 3F_2 \xrightarrow{\Delta} 3TeF_5OF + BF_3}$$

This reaction provides TeF_5OF in 80–95% yield at 100–115 °C after 1–3 days. Either stainless steel or Monel reactors may be used with the latter, giving consistently higher yields in shorter reaction times. Separation of byproducts, mainly BF_3 and TeF_5OH, is easily accomplished. Since commercial F_2 is the fluorinating agent, the need for synthesizing the hazardous $FOSO_2F$ is eliminated. To our knowledge this preparation of TeF_5OF is the first example of the formation of a hypofluorite involving the fluorinative scission of a boron–oxygen bond.

Experimental Section. Materials and Apparatus. Volatile materials were manipulated in a stainless steel vacuum line equipped with Teflon-FEP U-traps, 316 stainless steel bellows-seal valves, and a Heise Bourdon tube-type pressure gauge. Pentafluorotelluric acid was prepared from telluric acid, $Te(OH)_6$, and fluorosulfuric acid, HSO_3F.[1] Reaction of BCl_3 with excess TeF_5OH at ambient temperature provided $B(OTeF_5)_3$.[4] Spectroscopic measurements were performed with equipment and techniques previously described.[1]

Synthesis of TeF_5OF. Caution! While we have not encountered any difficulties or incidents in preparing and handling TeF_5OF, its hypofluorite nature demands treatment as a potentially violent oxidizer. Suitable safety precaustions must be followed.

In the dry-nitrogen atmosphere of the glovebox, a sample of $B(OTeF_5)_3$ (0.95 mmol) was weighed and transferred to a prepassivated 16-mL Monel pressure cylinder equipped with a Monel Hoke valve. The cylinder was transferred to the vacuum line, evaluated, and cooled to −196 °C, and F_2 (~7 mmol) was added. The closed cylinder was warmed to ambient temperature before being placed in an oven at 115 °C. After 24 h the cylinder was cooled to ambient temperature before it was cooled further to −196 °C (*hot* Monel should not be cooled directly to −196 °C since it may rupture catastrophically). The excess F_2 was pumped away through a scrubber, and then, while the reactor was allowed to warm from −196 °C to room temperature, the volatile products were separated by fractional condensation through a series of U-traps cooled at −78, −126, and −196 °C. In the lowest temperature trap were BF_3 and a little TeF_6 (1.05 mmol total), while the trap at −78 °C contained TeF_5OH (0.05 mmol). Retained in the trap cooled at −126 °C was pure TeF_5OF (2.68 mmol, 94% yield based on $B(OTeF_5)_3$). In all respects the properties of this material matched those reported.[1]

With use of the Monel vessel and a 100 °C reaction temperature for 22 h, the yield of TeF_5OF was 55%. This yield had increased to 95% when the reaction was examined after a total of 67 h at 100 °C. When a 30-mL stainless steel cylinder was employed as the reactor at 100 °C, the yield of TeF_5OF was 74% after 64 h and 80% after 83 h. At 115 °C in the stainless steel reactor, the hypofluorite was formed in 43% yield after 24 h and 81% after 51 h total. No unreacted $B(OTeF_5)_3$ remained at the conclusion of these reactions.

Acknowledgment. We gratefully acknowledge support for this work by the U.S. Air Force Office of Scientific Research under Contract F49620-81-C-0020. We are also grateful to Dr. L. R. Grant for helpful discussions.

---

(1) Schack, C. J.; Wilson, W. W.; Christe, K. O. *Inorg. Chem.* **1983**, *22*, 18.

(2) Cady, G. H. *Inorg. Synth.* **1968**, *11*, 155.

(3) Shreeve, J. M. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 119.

(4) Sladky, F.; Kropshofer, H.; Leitzke, O. *J. Chem. Soc., Chem. Commun.* **1973**, 134.

Rocketdyne, a Division of Rockwell
International Corporation
Canoga Park, California 91304

Carl J. Schack*
Karl O. Christe

Received May 25, 1984