data, further studies of a wider range of acetylene, olefin, and diazene derivatives are needed to extend our fundamental understanding of the factors which influence the electronic and molecular structure of this important class of small ring metallacyclic complexes.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. Computer time for the X-ray diffraction data analysis was provided by the West Virginia Network for Educational Telecomputing.

Oxidation States of Europium in Zeolites

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Received December 6, 1979

Rare-earth metal ions have proven to be particularly useful in zeolite catalysis, both as stabilizing ions and by virtue of their redox chemistry. In the research reported here, the europium Mössbauer spectra of hydrated and dehydrated europium-exchanged zeolites A, Y, and ZSM-5 have been studied. $Eu(OH)_2 \cdot H_2O$, used to ion exchange Eu^{2+} into the zeolites, immediately oxidizes to an Eu^{3+} complex in a deoxygenated aqueous solution. This same reaction occurs in the solid state for $Eu(OH)_2 \cdot H_2O$. An investigation into the role of europium in the thermolytic decomposition of water has been made, and the redox changes from the 3+ to the 2+ oxidation states of europium in zeolites Y and ZSM-5 have been confirmed by EPR. The Mössbauer isomer shifts are sufficiently sensitive to detect the difference in the chemical environment of Eu^{3+} as a consequence of oxidation by chlorine and oxygen. No evidence of Eu^{4+} has been found in an isomer shift range of ± 35 mm/s. Metal ions produced by dissolving europium metal in liquid ammonia can be exchanged into the zeolites to give an Eu^{2+} species as indicated by Mössbauer spectroscopy.

Introduction

Europium-exchanged zeolites are of interest because the rare-earth-exchanged zeolites are important as catalysts and because the crystallinity of the zeolites provides cation sites of a definite symmetry. A number of experiments have been performed in order to identify the structural and chemical properties of europium-exchanged zeolites. The presence of Eu^{4+} in zeolite A has been postulated on the basis of X-ray crystallographic evidence.[2,3] Electron paramagnetic resonance has been applied to study the cation locations and ligand coordinations of europium-exchanged mordenite and Y zeolite.[4] A process has been reported for thermolytically dissociating water by using europium-exchanged zeolites.[5] It is believed that europium changes back and forth between the 2+ and 3+ oxidation states in this thermolytic cycle. A Mössbauer study of europium-exchanged mordenite and Y zeolite has been previously reported.[6] In this study these materials were treated with flowing hydrogen at 450 °C which led to nearly complete reduction of Eu^{3+} to Eu^{2+}.

We present here the results of europium Mössbauer measurements on europium-exchanged zeolites A, Y, and ZSM-5 for calcined and hydrated samples. In addition, we show that the $Eu(OH)_2 \cdot H_2O$ compound is kinetically unstable. The postulated mechanism for the thermochemical decomposition of water catalyzed by europium-exchanged zeolites and the existence of europium(IV) are discussed. Finally, a new method for introducing europium(II) into zeolites is reported.

Experimental Methods

Preparation of Compounds. A. $Eu(OH)_2 \cdot H_2O$. The compound $Eu(OH)_2 \cdot H_2O$ was prepared according to the method of Bärnighausen.[7] The lemon yellow material precipitated from a mixture of 0.5 g of europium metal and 20 mL of 10 N NaOH. The reaction was carried out under a pure argon atmosphere by using Schlenkware. All water was distilled, deionized, and deoxygenated. The $Eu(OH)_2 \cdot H_2O$ was washed with deoxygenated ethanol, dried under vacuum, and subsequently stored in the dark in an argon-filled Vacuum Atmospheres drybox. All starting materials were purchased from Alfa Ventron Co.

B. Europium-Exchanged Zeolite A. In a Schlenk tube 4.5 g of NaA zeolite having a composition of $Na_{12}Al_{12}Si_{12}O_{48} \cdot 27H_2O$ was added to 200 mL of a saturated aqueous solution of $Eu(OH)_2 \cdot H_2O$. All solvents mentioned in this report had been distilled and deoxygenated. This reaction was carried out in the dark under an argon atmosphere while the mixture was stirred over a period of 6 days. The resulting zeolite was filtered through a medium frit in the middle of the Schlenk apparatus, the solvent was removed, and the product was then brought into the drybox and stored in the dark in a capped vial. During this procedure the europium-exchanged zeolite was not exposed to oxygen, the atmosphere, or light. Neutron-activation analysis showed that the hydrated A zeolite was 21.5% europium, corresponding to the approximate composition $Eu^{3+}_{3.5}Na_{1.5}Al_{12}Si_{12}O_{48} \cdot 27H_2O$.

C. Europium-Exchanged Zeolite Y. Approximately 2.0 g of zeolite NaY having a composition $Na_{56}Al_{56}Si_{136}O_{384} \cdot 256H_2O$ was added to 200 mL of a 0.1 N $EuCl_3 \cdot 6H_2O$ aqueous solution and exchanged while the mixture was stirred for 12 h in a round-bottomed flask. The resulting europium-exchanged zeolite was filtered through a medium frit and stored in a capped vial. Neutron-activation analysis showed that the hydrated Y zeolite was 14.8% europium, corresponding to

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(2) R. L. Firor and K. Seff, *J. Am. Chem. Soc.*, **100**, 976 (1978).
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the approximate composition $Eu^{3+}_{18}Na_2Al_{56}Si_{136}O_{384}\cdot 256H_2O$.

D. Europium-Exchanged Zeolite ZSM-5. ZSM-5 was prepared according to example 27 of Patent 3 702 886.[8] X-ray powder diffraction has confirmed the existence of the ZSM-5 zeolite which has an approximate composition of $(Na_2O)_{7.3}(Al_2O_3)_{8.3}(SiO_2)_{87.4}$. Approximately 2.0 g of ZSM-5 zeolite was added to 200 mL of a 0.1 N $EuCl_3\cdot 6H_2O$ aqueous solution and exchanged while the mixture was stirred for 12 h in a round-bottomed flask. The resulting europium-exchanged zeolite was filtered through a medium frit and stored in a capped vial. Neutron-activation analysis showed that the ZSM-5 zeolite was 9.7% europium, corresponding to the approximate composition $(Eu^{3+}_{0.66}Na_{0.14}O)_{7.3}(Al_2O_3)_{8.3}(SiO_2)_{87.4}$.

E. Europium-Exchanged Zeolites from Solutions of Europium Metal Dissolved in Liquid Ammonia. A simple apparatus consisting of two glass tubes at right angles to each other and separated by a glass frit was used in these experiments. A gas–vacuum stopcock was attached on both sides of the frit for vacuum filtering and ammonia gas flow into and out of the two tubes. A partial pressure of nitrogen gas was maintained in the apparatus throughout the experiments to exclude oxygen and water. One tube was charged with 0.25 g of europium metal while the other was loaded with 1.0 g of dehydrated zeolite in the drybox. Initially, liquid ammonia was condensed out on the side containing the europium metal by using a dry ice/acetone bath. The europium dissolved in the liquid ammonia, forming a solution having the characteristic deep blue color of alkali and alkaline-earth metals in ammonia.[9] This solution was vacuum transferred through the frit and onto the zeolite for periods from 2 to 12 h. The blue europium–liquid ammonia solution was then vacuum filtered off the zeolite, and the zeolite was further washed with fresh liquid ammonia and filtered. After the liquid ammonia filtrate was allowed to evaporate, the vessel was then evacuated and brought into the drybox. The exchanged zeolite was removed and stored in capped vials.

Physical Measurements. A. ^{151}Eu **Mössbauer Experiments.** Liquid nitrogen and room-temperature europium-151 Mössbauer spectra were obtained on a constant-acceleration spectrometer. Computer fitting of all the ^{151}Eu Mössbauer data to Lorentzian lines was carried out with a modified version of a previously reported program.[10] Attempts to fit the data to Gaussian lines were unsuccessful. All samples were loaded in polyethylene cylinders and sealed in a drybox with a mixture of beeswax and paraffin.

B. Q-Band Electron Paramagnetic Resonance EPR Experiments. EPR spectra were recorded on a Varian E-15 Q-band spectrometer.

C. Neutron-Activation Analyses. Neutron-activation analyses for determining the amount of europium and sodium in the europium-exchanged zeolites were performed by the Environmental Studies Department of the University of Illinois.

Results

It is noted that for a $^{151}SmF_3$ source the Mössbauer isomer shift for Eu^{2+} appears approximately between −15.0 and −12.0 mm/s and that the isomer shift for Eu^{3+} occurs around 0.0 mm/s.[11]

Mössbauer Spectra of $Eu(OH)_2\cdot H_2O$. The Mössbauer spectra of $Eu(OH)_2\cdot H_2O$ taken over a period of 2 weeks are shown in Figure 1A–C. Figure 1A shows the ^{151}Eu Mössbauer spectrum of $Eu(OH)_2\cdot H_2O$ after 6 days. The Eu^{2+} Mössbauer peak decays after 15 days to that shown in Figure 1B. Figure 1C shows that the material further loses more of its Eu^{2+} signal after 20 days. When the freshly prepared lemon yellow $Eu(OH)_2\cdot H_2O$ powder is immersed in deoxygenated water, it immediately turns white, and gas is given off. The Mössbauer spectrum of the white solid resulting from this treatment is shown in Figure 1D.

Mössbauer Spectra of $Eu(OH)_2\cdot H_2O$-Exchanged Zeolite A and Subsequent Chemical Treatments. When a saturated aqueous solution of $Eu(OH)_2\cdot H_2O$ is exchanged with zeolite A for 6 days, a white europium-exchanged zeolite results.

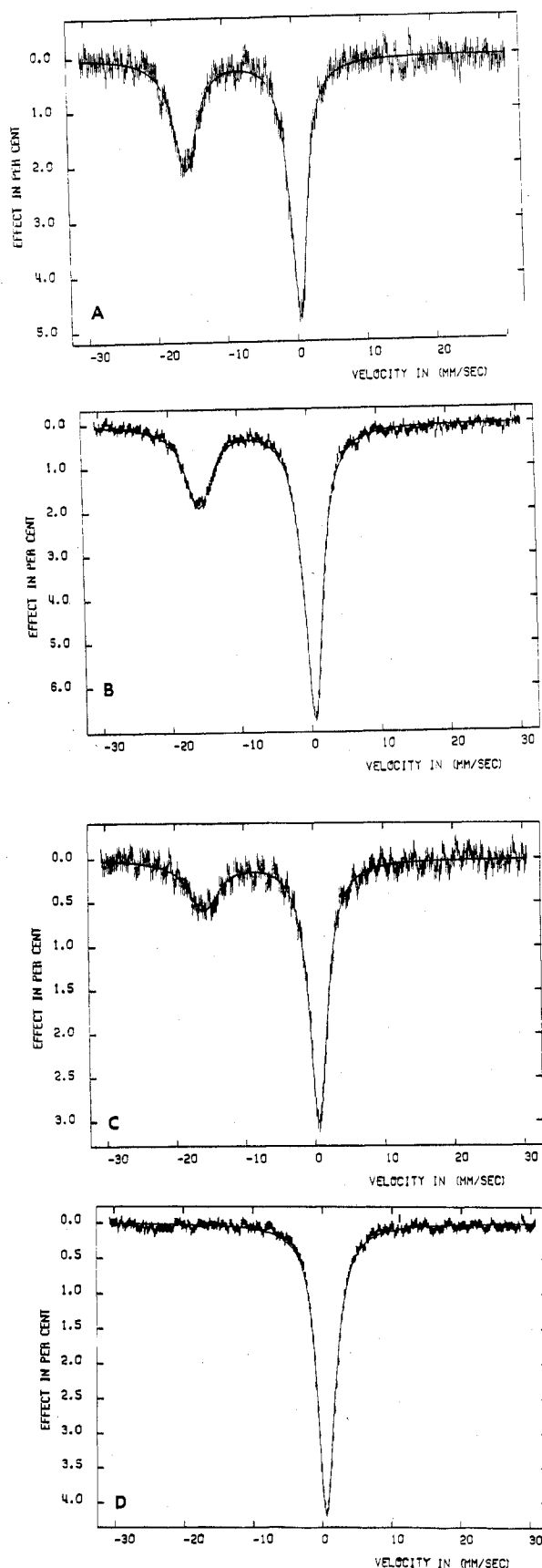(8) R. J. Argauer and G. R. Landolt, U.S. Patent 3 702 886.
(9) S. Salot and J. C. Warf, *J. Am. Chem. Soc.*, **90**, 1932 (1968).
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(11) "Mössbauer Effect Data Index", J. G. Stevens and V. E. Stevens, Eds., IFI/Plenum Press, New York, 1975.

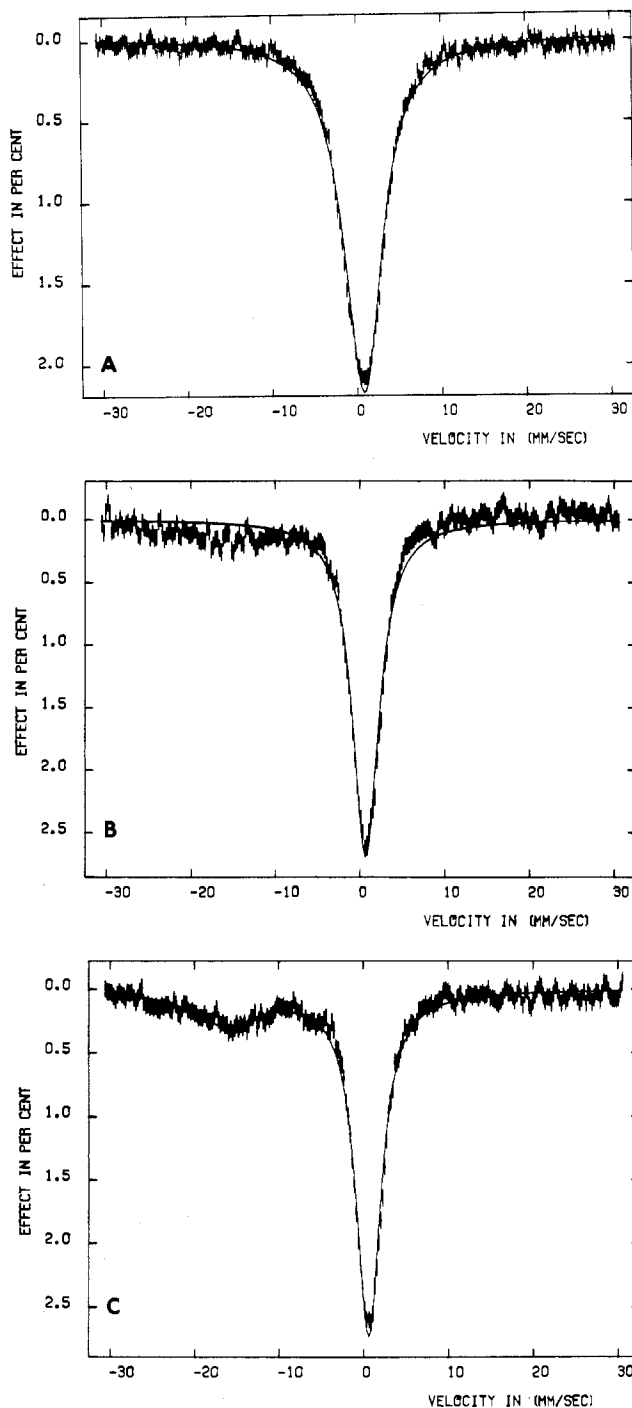**Figure 1.** Mössbauer spectra of $Eu(OH)_2\cdot H_2O$ after (A) 6 days, (B) 15 days, (C) 20 days, and (D) 1 day and exposure to deoxygenated water.

Figure 2. Mössbauer spectra of (A) hydrated europium A zeolite, (B) europium A zeolite previously heated to 375 °C, and (C) europium A zeolite previously heated to 400 °C.

Figure 2A shows the Mössbauer spectrum of this hydrated europium A zeolite. Q-Band EPR measurements confirm the presence of some Eu^{2+}. When this material is heated to 375 °C in a vacuum line with a pressure of 5×10^{-6} torr, an orange material is formed. The Mössbauer spectrum of this orange dehydrated europium zeolite given in Figure 2B shows no evidence of containing Eu^{2+}. However, the EPR spectrum confirms the presence of small amounts of Eu^{2+}. When the orange material is heated to 400 °C, a white color develops, and the spectrum in Figure 2C is observed. When the white europium-exchanged zeolite is dehydrated at 400 °C and subsequently treated with oxygen, the europium 2+ signal decays, and the 0.53 (1) mm/s isomer shift noted in Table I is observed. The oxygen-treated material was produced by

Table I. Europium-151 Mössbauer Parameters

	Eu²⁺		Eu³⁺	
compd[a]	δ,[b-d] mm/s	rel[e] area	δ,[b-d] mm/s	rel[e] area
Eu(OH)₂·H₂O (1A)	−15.6 (3)	38	0.54 (1)	62
(1B)	−15.7 (2)	28	0.57 (2)	70
(1C)	−15.8 (5)	25	0.58 (1)	75
hydrated EuA zeolite (2A)			0.58 (2)	100
dehydrated EuA zeolite (2B)			0.61 (3)	100
dehydrated EuA zeolite (2C)	−16.2 (2)	21	0.63 (2)	79
O₂-treated EuA zeolite			0.53 (1)	100
Cl₂-treated EuA zeolite			0.68 (2)	100
hydrated EuY zeolite			0.46 (2)	100
dehydrated EuY zeolite			0.45 (2)	100
hydrated Eu ZSM-5 zeolite			0.53 (3)	100
dehydrated EuZSM-5 zeolite	−16.3 (5)	15	0.02 (2)	85
europium–liquid ammonia Y zeolite (3)	−14.7 (1)	58	1.24 (4)	42
europium–liquid ammonia A zeolite	−13.5 (1)	14	0.93 (2)	86

[a] Information in parentheses refers to figures in this report. [b] Relative to SmF₃. [c] Error in last significant figure in parentheses. [d] All data reported are for 295 K. [e] Relative area is reported in percent.

treating the dehydrated 400 °C zeolite at room temperature with 760 torr of zeolitically dried high-purity oxygen for 1 h. The Mössbauer cell was loaded in this oxygen environment. The Mössbauer spectrum of this vacuum-dehydrated europium-exchanged zeolite A after 220 torr of chlorine gas was added for 1 h yields an isomer shift of 0.68 (2) mm/s. The Mössbauer cell was loaded in a chlorine environment, and it is noted that the chlorine-treated zeolite developed a light yellow-green color. It is further observed that the dehydrated europium-exchanged zeolite A material when heated to less than 30 °C can re-form the hydrated starting material if water is added to this system. The amount of Eu^{2+} as detected by EPR measurements is less than that observed for the hydrated starting material. Treatment with flowing hydrogen at 450 °C increases the amount of Eu^{2+}.

Europium-Exchanged Zeolites Y and ZSM-5. All hydrated $EuCl_3 \cdot H_2O$-exchanged zeolites produced Mössbauer spectra that showed only the incorporation of Eu^{3+} as evidenced by a single peak around 0 mm/s. When europium-exchanged Y zeolite is dehydrated up to 600 °C, there is no Eu^{2+} Mössbauer peak as has been previously reported.[12] Europium-exchanged ZSM-5, however, does show a small amount of Eu^{2+} on dehydration to 600 °C, at −16.3 (5) mm/s. Dehydrated europium Y zeolite is gray, and the dehydrated ZSM-5 turned black. EPR spectra of both dehydrated Y and ZSM-5 zeolites, however, confirm the presence of small amounts of Eu^{2+}.

Europium-Exchanged Zeolites via Metallic Europium Dissolved in Liquid Ammonia. This procedure was used to exchange europium into zeolites A, X, and Y. In the case of zeolite A, a calcium-exchanged dehydrated zeolite A was used as starting material. This material turned a light orange and did show a Eu^{2+} Mössbauer peak that was less pronounced than any of the other europium-exchanged A zeolite materials. The Mössbauer spectrum for a 6-h metallic europium–liquid

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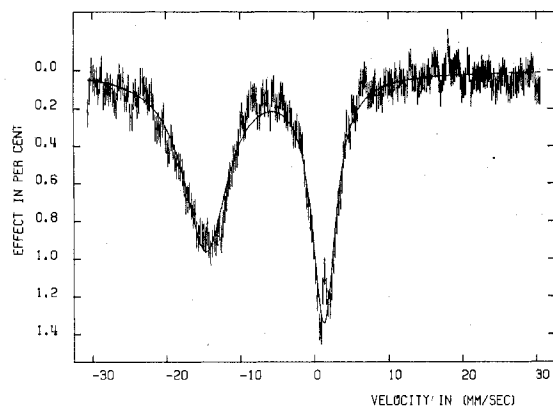
Figure 3. Mössbauer spectrum of NaY zeolite exchanged with europium dissolved in liquid ammonia.

ammonia exchange in zeolite Y is shown in Figure 3. The exchanged zeolite was flesh colored. When the sodium salt of zeolite X is used, the zeolite first turns purple and gives a 13-line EPR spectrum superimposed on a large broad spectrum. Infrared analysis of these types of compounds reveals broad bands of 3000 and 1600 cm^{-1} as well as the characteristic zeolite-framework bands. All of these materials are very air sensitive and when exposed in a drybox (O_2 < 1.0 ppm, H_2O < 0.1 ppm) for periods greater than 15 min show some decomposition. The isomer shifts for all of the compounds mentioned in this section are given in Table I.

Mössbauer Spectra of Europium(III)-Exchanged Zeolite A. When a 0.1 M solution of europium trichloride is exchanged in the presence of zeolite A for 6 days, a white europium-(III)-exchanged A zeolite results. Figure 4A shows the Mössbauer spectrum for this material. On dehydration of this material to 400 °C a white solid is obtained which shows the characteristic Mössbauer spectrum of Figure 4B. Figure 4C shows the Mössbauer spectrum of the zeolite material of figure 4B which has been rehydrated.

Discussion

Eu(OH)$_2$·H$_2$O. Our data reemphasize the observation of Bärnighausen[7] that Eu(OH)$_2$·H$_2$O decomposes to Eu(OH)$_3$ in time as they observed by X-ray Guinier photographs. After a period of 8 weeks the Eu^{2+} Mössbauer signal is nonexistent. The decomposition is due to eq 1. This decomposition occurs

$$2Eu(OH)_2·H_2O \rightarrow 2Eu(OH)_3 + H_2\uparrow \qquad (1)$$
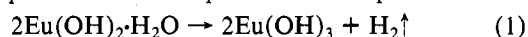
in the solid state and is enhanced by the addition of water to the system. The isomer shift of Eu(OH)$_3$ [0.58 (1) mm/s] is in good agreement with that reported by Colquhoun and co-workers.[13] Their isomer shift was reported as 0.58 (4) mm/s.

Europium-Exchanged Zeolite A. The conditions we used for studying the exchange of zeolite A with Eu(OH)$_2$·H$_2$O were essentially the same as those reported by Seff and co-workers.[2,3] Two differences are that we have used powdered zeolites and they have used single crystals and that their ion-exchange process involved a flow system whereas ours involved an alternative procedure. The colors of the hydrated and dehydrated europium-exchanged zeolite A species that we observe are consistent with theirs except for the chlorine-treated zeolite. Our observations indicate that approximately 95% of the europium in the hydrated starting material is actually in the 3+ oxidation state and that dehydration does not induce large amounts of Eu^{2+}. The EPR data show that the orange material contains both oxidation states of europium. When oxygen and chlorine are added to the europium-ex-
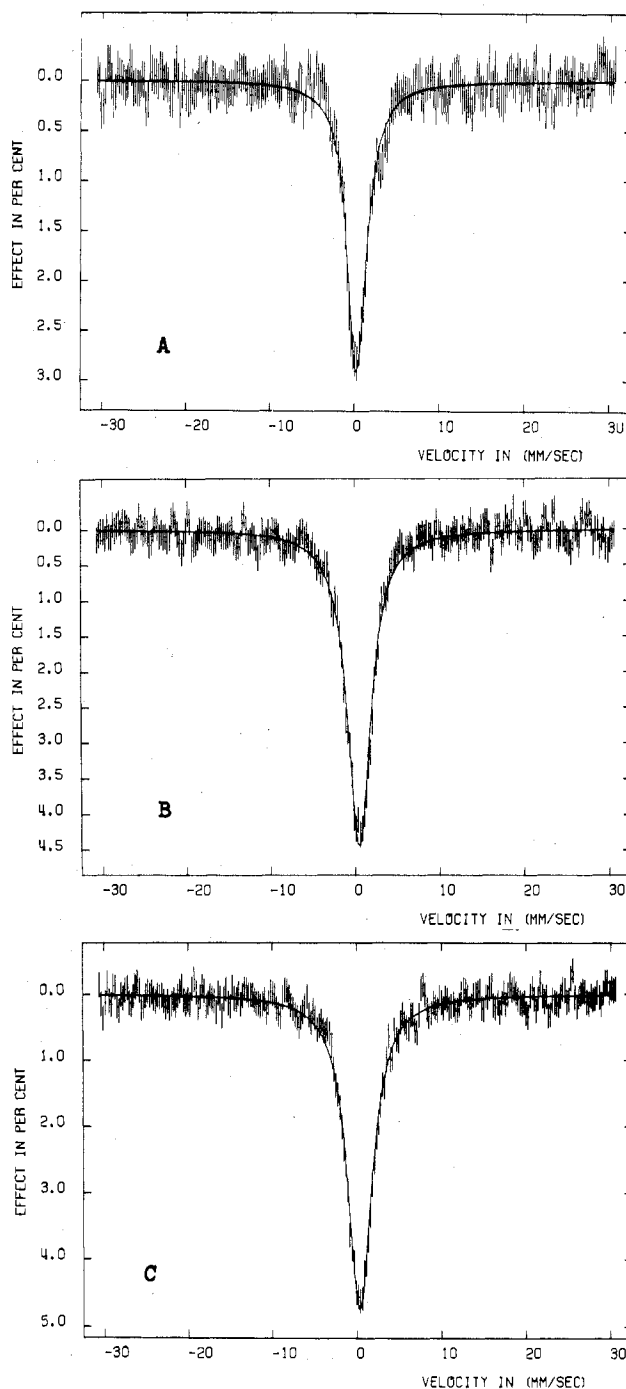

Figure 4. Mössbauer spectra of NaA zeolite exchanged with aqueous europium trichloride: (A) hydrated europium A zeolite; (B) dehydrated europium A zeolite at 400 °C; (C) rehydrated europium A zeolite.

changed zeolite A, there is no evidence in our Mössbauer spectra that Eu^{4+} is formed but rather that Eu^{3+} is formed as has been suggested by Jørgenson.[14]

Cyclic Thermolysis of Water. Kasai and Bishop[5] have postulated that trivalent europium cations in crystalline zeolite structures undergo interactions with water molecules where the Eu^{3+} cations are reduced and the water molecules are decomposed with the evolution of oxygen. Hydrogen is evolved by reoxidizing the bivalent europium cations to their original Eu^{3+} state. In their studies, hydrogen and oxygen have been observed when the dehydration temperature is at least 200 °C

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and less than the crystal destruction temperature of the particular zeolite.

Our Mössbauer experiments have provided evidence that Eu^{2+} is generated on dehydration of europium-exchanged A and ZSM-5 zeolites. The amount of Eu^{2+} conversion, however, is very low. Successive reduction–oxidation cycles of the Eu^{3+} and Eu^{2+} oxidation states of europium-exchanged zeolite Y using oxygen have been observed with the EPR technique.[4] We are presently investigating in detail the EPR of the systems mentioned in this paper.

Europium-Exchanged Zeolites Produced via Metallic Europium Dissolved in Liquid Ammonia. We have demonstrated that europium can be exchanged into the zeolite framework in the Eu^{2+} oxidation state in zeolites A, X, and Y. In the case of zeolite X, we initially observed a purple color and a 13-line EPR spectrum indicative of Na_4^{3+} color centers. This color center has been formed in a number of other ways, including sodium-vapor reduction[15] and γ-ray irradiation.[16] This color center decays in time if left exposed in the drybox atmosphere and forms a tan product which gives a Mössbauer spectrum that reveals europium in the 2+ and 3+ states. For ion-exchange periods of longer than 2 h, color centers were not observed probably because the sodium ions are being replaced by europium ions. Color centers were not observed in the reactions of zeolite A or Y presumably due to the facts that zeolite A has a smaller cage size and that zeolite Y has fewer Na^+ ions per large cage. Europium–ammonia solutions have been reported before.[9,17,18] Mössbauer studies[18] have shown that at -50 °C over long periods of time Eu^{2+} in liquid ammonia gradually decomposes to Eu^{3+}. This would account for the Eu^{3+} peak observed in Figure 3 for the europium–liquid ammonia exchanged zeolite Y. The infrared results suggest that NH_3 and probably NH_2 are present in the zeolites after these liquid ammonia preparations.

The data in Table I show that a wide range of isomer shifts exists for both the Eu^{2+} and the Eu^{3+} oxidation states. The isomer shift of the oxidized $Eu(OH)_2 \cdot H_2O$ species of Figure 1C is the same as the value reported for $Eu(OH)_3$, which is 0.58 mm/s. We do not observe major changes in isomer shift of the EuA or EuY zeolites on dehydration. The isomer shifts of 0.53 (1) and 0.68 (2) mm/s for the oxygen- and chlorine-treated zeolite A materials are in line with the relative oxidizing ability of these reagents. The computer simulation for the europium–liquid ammonia Y zeolite suprisingly leads to much more positive isomer shifts for both Eu^{2+} and Eu^{3+}

entities than for europium salt solution preparations. The cause of the more positive isomer shifts for both Eu^{2+} and Eu^{3+} of the liquid ammonia exchanged samples indicates that there is a greater degree of charge transfer from the europium to the NH_3 ligands than to oxygen ligands (either H_2O or framework oxygen). Since the EPR spectra of these systems are so broad, there is no chance of observing superhyperfine structure from the NH_3 ligands; even the hyperfine structures from the ^{151}Eu and ^{153}Eu nuclei are obscured in these types of materials. Similar behavior was observed for the calcium A zeolite europium–liquid ammonia preparation.

Europium(III)-Exchanged Zeolite A. The last set of Mössbauer spectra of Figure 4 show that on dehydration no significant amount of Eu^{2+} is generated from the starting Eu^{3+} hydrated zeolite. This means that *some* Eu^{2+} (15% maximum) is exchanged into zeolite A by way of the Seff procedure. EPR experiments unequivocally show the presence of Eu^{2+}, indicating that the small amount of europium(II) is actually stable at room temperature in the zeolite. If the system were reversible, on rehydration of the Eu^{3+}-exchanged dehydrated zeolite the percent effect should decrease[12] from the dehydrated case and be the same as the original hydrated material. The data in Figure 4C show this not to be the case, and this may indicate irreversible europium ion migration to the small cages. In any event, the europium ions on rehydration are unwilling to change their size and location. This may influence the catalytic water thermolysis scheme for zeolites A and Y.

Conclusion

Various authors[19,20] claim that europium(II) aqueous solutions are stable. This is true only for the case of highly acidic conditions.[21,22] We have noted that the compound $Eu(OH)_2 \cdot H_2O$ is kinetically unstable and is rapidly decomposed with the addition of water. We have provided evidence that europium does change from oxidation state III to II in crystalline zeolites on dehydration. We have found no evidence within the limits of our detection of europium(IV) in any of the experiments that we have described. In addition, we have developed a new method of introducing europium(II) into zeolites.

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