JOURNAL OF CATALYSIS **114**, 53–57 (1988)

Hydrolysis of Europium Cations in Zeolite X: A Fourier Transform Infrared Spectroscopic Study

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Received May 15, 1987; revised April 21, 1988

A series of thermally activated europium-exchanged X zeolites with comparable cation loadings have been characterized by infrared spectroscopy. The distribution of surface hydroxyl species observed following sample dehydration was found to be influenced by the preparation conditions employed during ion exchange, and increasing time of contact between the exchange solution and the parent NaX sample resulted in an increase in the abundance of surface hydroxyl groups. On the basis of the observed infrared data, it is proposed that the surface hydroxyl species arise as a consequence of hydrolytic reactions occurring within the zeolite cages during ion exchange and not as a consequence of thermally promoted hydrolysis. © 1988 Academic Press, Inc.

INTRODUCTION

Rare earth (RE^{3+}) ion-exchanged faujasite zeolites enjoy a position of considerable technological importance due to their use as cracking catalysts (*1*). The catalytic activity of these materials stems, at least in part, from the formation of framework and extra-framework hydroxyl species within the zeolite channels (*2–10*). These surface hydroxyls are generally considered to arise following thermally induced hydrolysis of the RE^{3+} ions as water molecules associated with the cations are desorbed at temperatures in excess of 570 K (3). Protons thus formed are thought to condense with framework oxygen atoms, resulting in the formation of acidic Si–OH surface species.

The aqueous solution chemistry of RE^{3+} cations such as Eu^{3+} is also influenced by various pH-dependent hydrolysis reactions (*11–13*). The principal hydrolytic complex in acidic solutions of Eu^{3+} is thought (*11*) to be $[Eu(OH)]^{2+}$, although the cation appears to resist hydrolysis when the pH remains below 5–6. A precipitate of $Eu(OH)_3$ generally forms when the pH of solutions containing Eu(III) ions exceeds ca. 6 (*11*).

The presence of unique electrostatic and microporous environments within the internal structure of zeolites suggests that different hydrolytic behavior may be expected for RE^{3+} ions within zeolite matrices that are in contact with bulk aqueous solutions. Our studies of actinide speciation (where decisive identification of hydrolytic species is possible) within synthetic faujasite zeolite frameworks have revealed direct evidence for the formation of hydrolyzed uranium(VI) species within the zeolite channels during ion exchange that would not be expected to be stable at the pH of the ambient aqueous medium (*14*). These findings suggest that the formation of zeolite hydroxyl groups, as a consequence of RE^{3+} hydrolysis, may proceed to some extent prior to zeolite dehydration.

In this study, we report the results of an infrared spectroscopic study of surface hydroxyl formation within the channels of EuX zeolites. We also present evidence

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0021-9517/88 $3.00

illustrating the role of the exchange solution and associated interchannel hydrolysis of Eu^{3+} in promoting the formation of the surface hydroxyl species observed following dehydration of the zeolites.

EXPERIMENTAL

Sample preparation. Zeolite NaX was obtained from Union Carbide. Europium trichloride hexahydrate (99.99%) was an Aldrich product. Prior to ion exchange, the parent NaX sample was stirred in aqueous NaCl (0.1 mol dm^{-3}) for ca. 48 h, and then washed with an acetate buffer solution (pH 4.5–4.7) to minimize hydrolysis of the Eu^{3+} cations during ion exchange (*15*). The pretreated samples were then stirred in solutions containing an excess of $EuCl_3$ (0.05–0.09 mol dm^{-3}) for varying lengths of time, as indicated in Table 1. During exchange, the solutions were purged with high-purity nitrogen gas to exclude CO_2. The resulting zeolites were thoroughly washed with fractionated water, and dried in air at 330–370 K.

The EuX zeolites were analyzed by neutron activation and energy-dispersive X-ray analysis (EDAX), and the compositions calculated on the basis of these data are included in Table 1. Since all zeolites studied exhibited comparable metal ion loadings, the individual ion-exchanged products are identified in subsequent discussion by appending the length of time required to prepare the sample; e.g., EuX-0.35 refers to a sample that was ion-exchanged for 0.35 h.

Samples to be examined in infrared experiments were pressed into self-supporting wafers of mass 10–15 mg and diameter 1.3 cm. Generally, four samples supported in a metal carriage were pretreated simultaneously (see below) in a modified version of the cell previously described (*17*). The zeolites were carefully dehydrated *in vacuo* at increasing temperatures to a final 730–770 K, and were heated overnight in oxygen at this temperature. The excess oxygen was then removed by evacuation at 770 K. This treatment has been reported to lead to a zeolite incorporating Eu(III) species (*16*), even though dehydration of EuX or EuY samples at temperatures in excess of 570 K *in vacuo* initially leads to the formation of Eu(II) species within the zeolite cation sites (*16*).

Equipment and techniques. Infrared spectra were recorded on a Nicolet 8000

TABLE 1

Relative Intensities[a] of Bands Assigned to Surface Hydroxyl Species in the FT-IR Spectra of EuX Zeolites, Including Chemical Analyses, Surface Areas, and Unit Cell Dimensions of Samples

Zeolite code[b]	Nominal surface area (m^2 g^{-1})	Unit cell (nm)	Composition[c]	Extra-framework Al–OH *I*(3680)	Framework Si–OH *I*(3650)	Framework Si–OH *I*(3580)	Si–OH or Eu–OH[d] *I*(3500)
EuX-0.35	785	2.503	$Na_{24}Eu_{15}X$	1.2	0.4	0.7	1.5
EuX-1.3	—	—	$Na_{21}Eu_{18}X$	1.3	0.6	0.8	1.6
EuX-3.5	—	—	$Na_{20}Eu_{17}X$	1.3	0.9	1.1	2.1
EuX-18	792	2.502	$Na_{22}Eu_{17}X$	1.4	2.8	1.7	2.2

[a] Intensities are quoted relative to that of the band at 3746 cm^{-1}. All relative intensities were determined from peak heights above the background, and include an estimated error of ±0.1.

[b] See Experimental for an explanation of sample codes.

[c] Analyses for Na and Eu calculated on the basis of neutron activation and semiquantitative EDAX data. Analyses for Al and Si calculated on the basis of EDAX data only. X = framework composition, which was found in all cases to be $(AlO_2)_{79}(SiO_2)_{113}$.

[d] Band assignments taken from Refs. (*2–10, 18–21*).

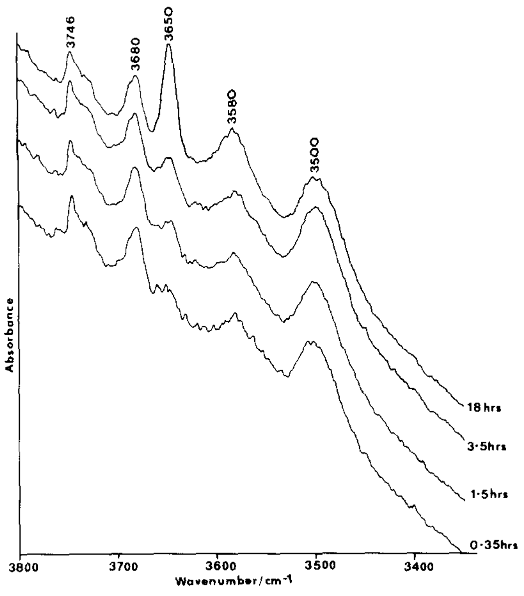

FIG. 1. Infrared spectra of EuX zeolites (following activation at 770 K), showing the effect of increasing duration of ion exchange on the distribution of surface hydroxyl species. From top to bottom: EuX-18, EuX-3.5, EuX-1.3, EuX-0.35.

FT-IR spectrometer at a resolution of 2 cm^{-1}. The spectrometer was equipped with an MCT detector cooled to 77 K. In addition to bands above 3500 cm^{-1} arising from surface hydroxyl species (Fig. 1), a number of extremely weak bands assigned to surface carbonate or bicarbonate species were also observed in the region 1300 to 1600 cm^{-1}. These latter species do not appear to be associated with the hydroxyl bands reported in Fig. 1, since the observed changes in the relative intensities of hydroxyl bands (Table 1) do not correlate with the minor changes in intensity observed for the bands assigned to the carbonate or bicarbonate species.

Selected samples were also examined by scanning electron microscopy, X-ray diffraction, and nitrogen adsorption. Nitrogen adsorption experiments were performed on a Micromeritics Accusorb 2100E for samples labeled EuX-0.35 and EuX-18, and the calculated surface areas are included in Table 1. The values obtained (785 and 792 m^2/g dry wt, respectively) effectively coincide with values previously reported by Eberly and Kimberlin (*2*) for synthetic faujasite exchanged with Eu(III) ions (789 m^2/g), and confirm that no significant blocking of the zeolite pores had occurred during ion exchange. The unit cell parameters of EuX-0.35 and EuX-18 (2.503 ± 0.002 and 2.502 ± 0.002 nm, respectively, Table 1) were comparable to that of the parent NaX sample (2.501 ± 0.002 nm).

RESULTS AND DISCUSSION

The FT-IR spectra of activated EuX-0.35, EuX-1.3, EuX-3.5, and EuX-18 over the range 3800 to 3400 cm^{-1} are presented in Fig. 1. The spectra exhibit broad bands with maxima centered at 3500, 3580, 3645–3650, 3680, and 3746 cm^{-1}. Additional weaker bands (neglected in subsequent discussion) may also be observed as shoulders to these stronger bands. The assignments of hydroxyl bands in the infrared spectra of REX, REY, and HY zeolites have been discussed by a number of authors (*2–10, 18–21*), and the proposed assignments of bands in Fig. 1 are listed in Table 1.

The bands at 3746, ca. 3650, 3580, and 3500 cm^{-1} in Fig. 1, are common features of the spectra of REX zeolites (*3, 10*). The 3746 cm^{-1} band is generally assigned either to siliceous impurities occluded within the zeolite cages or to hydroxyl groups terminating the semi-infinite zeolite lattice (*3, 4*). Consequently, its intrinsic intensity would be expected to remain constant for a series of EuX zeolites prepared from the same parent NaX sample; i.e., it may be employed as an internal standard for monitoring changes in the observed intensities of other hydroxyl bands. The additional bands at ca. 3650 and 3580 cm^{-1} are generally considered to arise following thermolysis of the RE^{3+} cations (see Introduction), and have been assigned to framework Si–OH (silanol) species (*10*). The spectra of zeolites HX and HY are also characterized by bands associated with surface silanol species at ca. 3650 and 3550–3600 cm^{-1} (*9*).

REX and REY zeolites have also been

found to exhibit a band in the region 3470 to 3520 cm^{-1}, which has no counterpart in the spectra of HX or HY (*2*). Since the wavenumber of this band varies with the nature of the RE^{3+} cation, it has been assigned to RE-OH species (formed as a result of cation thermolysis) by Eberly and Kimberlin (*2*). This assignment was disputed by Jacobs and Mortier (*9*), who assigned the band at 3525 cm^{-1} in the spectrum of La-exchanged faujasite to framework hydroxyl species residing in site $S_{I'}$, on the basis of electronegativity calculations. Consequently, the 3500 cm^{-1} band in the spectra presented in Fig. 1 may be assigned to either framework (Si–OH) or extra-framework (Eu–OH) hydroxyl species.

The band observed at 3680 cm^{-1} in Fig. 1 is not a common feature of the spectra of activated RE- or H-faujasite zeolites. A corresponding band has been previously reported in the spectra of both hydrothermally treated LaY (*6*) and ultrastable Y (USY) zeolites (*5*). In these latter cases, the band is generally assigned to A1–OH species formed following leaching of framework aluminum. The emergence of the 3680 cm^{-1} band in the spectra of Fig. 1 is thus considered to reflect the removal of small amounts of framework aluminum species either during the common pretreatment of all parent zeolite samples with pH 4.5–4.7 buffer or during subsequent ion exchange in acidic $EuCl_3$ solutions (see Experimental). Consistent with this interpretation, no substantial variations in its relative intensity were observed across the series of zeolites studied (Fig. 1 and Table 1). In contrast, the bands at ca. 3650 and 3580 cm^{-1} exhibit substantial changes in relative intensity across the series EuX-0.35 to EuX-18.

The samples do not appear to have sustained structural damage, since they still exhibit the high surface areas generally expected for REX zeolites (Table 1). In addition, the unit cell parameters of EuX-0.35 and EuX-18 (2.503 ± 0.002 and 2.502 ± 0.002 nm, respectively) were virtually coincident with that of the parent NaX sample (2.501 ± 0.002 nm), suggesting that the framework aluminum content was not significantly modified by the pretreatment or ion-exchange conditions employed (*3*).

The variations in the relative intensities of bands observed in Fig. 1 are summarized in Table 1. The intensities of the hydroxyl bands at ca. 3650, 3580, and 3500 cm^{-1} are found to increase at differing rates across the series EuX-0.35 to EuX-18, with the most dramatic variations in relative intensity being observed for the ca. 3650 cm^{-1} band. All spectra reported in Fig. 1 were obtained from samples that were activated simultaneously within the same cell under identical conditions. In addition, since all samples have comparable Eu(III) and Na^+ loadings [17 to 18 Eu(III) cations per unit cell, Table 1] with the exception of EuX-0.35 [15 Eu(III) cations per unit cell] the observed changes cannot be attributed to variations in metal ion content. In particular, if the acidic silanol species characterized by the band at ca. 3650 cm^{-1} were formed as a result of thermally induced hydrolytic processes, then the relative intensity of the band would be expected to remain largely unchanged between samples with comparable metal ion loadings.

The key conclusion arising from the data summarized above is that thermally induced dissociation of residual zeolitic water molecules during activation is not primarily responsible for the formation of the surface hydroxyl species. In particular, the 3650 cm^{-1} band appears with very low intensity in the spectrum of EuX-1.3 (Fig. 1 and Table 1). In contrast, its intensity is increased about fivefold in the spectrum of EuX-18, even though these zeolites have comparable Na^+ and Eu(III) loadings (Table 1). The major feature distinguishing the individual zeolites is the duration of the initial ion-exchange reactions (Table 1). These results are considered to reflect the importance of the kinetics of hydrolytic processes occurring within the zeolite channels during ion exchange in determining cation and framework speciation. In particular, the apparent influence of initial ion-exchange conditions on the relative intensity of the band at ca. 3650 cm^{-1} in the spectra of dehydrated samples would appear to stem from an increasing extent of cation hydrolysis with increasing time of exposure to the aqueous exchange medium. Increasing Eu(III) hydrolysis is also reflected by the increasing relative intensities of the 3580 and 3500 cm^{-1} bands.

The usual criterion employed to assess the extent of cation hydrolysis in multivalent cation-exchanged zeolites involves a comparison of the formal cationic and framework anionic charge equivalents (*22*). Thus, if the total apparent cationic charge (determined from the metal ion content) is numerically equivalent to the formal negative framework charge (calculated on the basis of the framework aluminum content), it is generally assumed that cation hydrolysis has not occurred during ion exchange. However, hydrolysis may result in the replacement of hydrated Eu^{3+} cations (residing in zeolitic cation sites) by mononuclear or polynuclear species within which the total charge of the cations has been reduced by the hydrolysis process. Some or all of the protons released during hydrolysis may occupy cation sites (and subsequently form framework hydroxyl species associated with the bands observed at 3650 and 3580 cm^{-1}) to restore the framework/cation charge balance, as illustrated by

$$(Na^+)_{(86-3x)}([Eu(H_2O)_n]^{3+})_x\mathbf{F} \rightarrow$$
$$(Na^+)_{(86-3x)}([Eu(OH)(H_2O)_{(n-1)}]^{2+})_x(H^+)_x\mathbf{F}$$

where **F** represents the zeolite framework. In this way, the metal ion content of the system may remain unchanged, even following extensive hydrolysis of the rare earth cations.

ACKNOWLEDGMENTS

We thank the Natural Sciences and Engineering Research Council of Canada for the equipment employed during this study. One of us (J.R.B.) also acknowledges financial assistance in the form of an Australian Commonwealth Postgraduate Research Student Award.

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