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ABSTRACT

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A STUDY OF THE REDOX MECHANISM

OF EXCHANGED ZEOLITES

by /

K.M.E. Miedzinska

A report submitted to the Department
of Chemistry in partial fulfilment of
the requirements for the degree of
Master of Science.

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ABSTRACT

Evidence was found that the Cr(III)/Cr(II) and Fe(III)/Fe(II) redox cycles previously described to occur upon dehydration and rehydration of exchanged zeolites 13X and Y52, do not in fact occur. Data suggests dimerization of the metal ion at high levels of exchange. Bridging provided by the lattice could stabilize these dimers and lead to reduction at very low temperatures. Evidence indicates irreversible formation of new lattices.

TABLE OF CONTENTS

Acknowledgements.....	1
Abstract.....	11
Table of Contents.....	111
List of Figures.....	1v
List of Tables.....	v
INTRODUCTION.....	1
Building Blocks.....	5
Cation Exchanged Zeolites.....	17
Dehydration of Zeolites.....	18
EXPERIMENTAL.....	21
Materials.....	21
Instruments.....	21
Sample Notation.....	23
Preparation of Exchanged Zeolite.....	23
Preparation of 1-Cr ²⁺ -(13X) ¹ C.....	27
Preparation of 2-Cr ²⁺ -(13X) ¹ C.....	29
Dehydration of Exchanged Zeolites.....	31
Rehydration of Exchanged Zeolites.....	31
Digestion of Exchanged Zeolites.....	32
Preparation of Reagents for Sodium Analysis.....	32
Sodium Analysis.....	32
Molecular Formulas and Weights.....	33
Percentage Exchange.....	33
Thermogravimetric Analysis.....	37
Differential Thermal Analysis.....	37
X-Ray Crystallography.....	44
Magnetic Susceptibilities.....	45
Infrared.....	48
CONCLUSIONS.....	54
REFERENCES.....	57

LIST OF FIGURES

FIGURE 1	The projection of Al + Si atoms in the sodalite cages....	4
FIGURE 2	The structure of faujasite.....	7
FIGURE 3	Idealized projection and section through a sodalite unit.	8
FIGURE 4	Apparatus for the exchange of Cr(II).....	28
FIGURE 5	Thermogravimetric analysis spectra of zeolite 13X and chromium exchanged 13X.....	38
FIGURE 6	Differential thermal analysis spectra of zeolite 13X and chromium exchanged 13X.....	39
FIGURE 7a	Infrared spectra of zeolite 13X and chromium exchanged 13X, 4000-1500 cm^{-1}	49
FIGURE 7b	Infrared spectra of zeolite 13X and chromium exchanged 13X, 1800-800 cm^{-1}	50

LIST OF TABLES

TABLE 1	Properties of Selected Zeolites.....	3
TABLE 2	Assignments of Cations and Water Molecules in Hydrated Faujasite Zeolites.....	12
TABLE 3	Assignments of Cations and Water Molecules in Dehydrated Faujasite Zeolites.....	13
TABLE 4	Zeolite Infrared Assignments, cm^{-1}	16
TABLE 5	Preparation of Chromium Exchanged Zeolites 13X and Y52.	24
TABLE 6	Preparation of Iron Exchanged Zeolites 13X and Y52.....	25
TABLE 7	Atomic Absorption Heating Modes.....	34
TABLE 8	Analysis Results.....	35
TABLE 9	Molecular Formulas, Weights and Percentages Exchanged..	36
TABLE 10	Differential Thermal Analysis Characteristics.....	40
TABLE 11	Magnetic Susceptibilities and Effective Moments of Exchanged Zeolites.....	46
TABLE 12	Infrared Spectral Characteristics.....	51

INTRODUCTION

In this age of energy shortages there is a movement towards finding a recyclable energy source. A great deal of interest has been taken in the use of zeolites in a variety of manners. Recently this interest has focussed on the support of transition metal ions within a zeolite cage (1-9) due to the possibility of stabilization of unusual oxidation and/or coordination states inside the zeolite framework (10,11).

The importance of zeolites in this field stems from the ability of small molecules to penetrate the intracrystalline structure and travel freely inside the channels. This requires that the critical dimension (kinetic diameter, σ) (12) of the travelling molecule should be smaller than the effective pore opening of the zeolite. Otherwise the molecule is excluded from the intracrystalline voids or, once inside, it exhibits only restricted motion (13).

Due to the complexity of its physical properties, there exist various⁺ general definitions of a zeolite. One, universally accepted, is as follows (14):

"a zeolite is an aluminosilicate with a framework structure enclosing cavities occupied by large ions and water molecules, both of which have considerable freedom of movement, permitting ion-exchange and reversible dehydration."

The framework structure consists of corner-linked tetrahedra in which the oxygen atoms lie at the corners and the small (T) atoms lie in the centre. The T sites of all natural zeolites are dominated by Al and Si atoms. The large ions in the zeolite cavities are mono- or di-valent. The principal species (Na, Ca, K, Mg or Ba) reflect the geochemical abundance in the environment.

The two zeolites involved in this work are 13X and Y52. Both X and Y are synthetic zeolites which have the same framework topology as faujasite. The general faujasite has a range of compositions. The synthetic analogues X and Y are synthesized in Na-bearing systems and have the composition

where p ranges from 96 to 74 for X and 74 to 78 for Y while q drops from about 270 to 250 as Al decreases. The water contents have been rounded to integral values, but since as a rule the water contents vary continuously with relative pressure and also with temperature, these values though near, are not necessarily exact saturation uptakes (18).

The above zeolites are considered the most porous and open, with pores into which molecules can be introduced after dehydration (see Figure 1).

TABLE 1 Properties of Selected Zeolites ^a

Name	Crystallographic Data	Selected Chemical Composition
Faujasite	isometric <u>a</u> 24.5 Å Fd3m	~Na ₁₃ Ca ₁₁ Mg ₉ K ₂ Al ₅₅ Si ₁₃₇ O ₃₈₄ ·235 H ₂ O
X	isometric <u>a</u> 25.0 Å	Na ₈₆ Al ₈₆ Si ₁₀₆ O ₃₈₄ ·264 H ₂ O
Y	isometric <u>a</u> 24.7 Å	Na ₅₆ Al ₅₆ Si ₁₃₆ O ₃₈₄ ·250 H ₂ O

^a References 15, 16 and 17

Crystallization of zeolites under laboratory conditions involves producing a highly supersaturated aqueous solution with the appropriate composition at a relatively low temperature range of 0° to 300°C. The actual product under these conditions is determined by kinetic factors. Thermodynamic equilibrium may be intirely irrelevant, thus enabling modification of the reactants and the physical conditions in order to modify the chemical composition (e.g. SiO₂/Al₂O₃ ratio), physical properties (e.g. grain size) or to produce new zeolites. An extensive discussion of synthesis conditions of important systems (such as Na₂O-Al₂O₃-SiO₂-H₂O) can be found in various patents and in Chapter 4 of Breck (12).

The projection of Al + Si atoms in the sodalite cages of faujasite centred on the (011) plane. The free dimensions and effective continuity of the channel are shown.

FIGURE 1 (18)

An extensive review of data regarding the properties of the aluminosilicate framework, the positions of cations and molecules and tables of cation distribution for structures determined before 1970 can also be found in Breck (12) and Smith (19).

X and Y zeolites grow only from a system with lower Al_2O_3 than their own composition.

The stability of the aluminosilica framework has been questioned as most studies provide evidence that Al can be removed without complete loss of crystallinity. The literature is confusing at this point, but it is known that both dehydration and ion-exchange may result in a framework richer in Si (i.e. poorer in Al) or in a complete breakdown of the framework.

Building Blocks - Simple Hydrates

In order to place the results of this work in perspective one must first build a picture of the simple hydrated and dehydrated zeolites 13X and Y52.

The molecular formulas of the hydrated 13X and Y52 zeolites are (respectively)

As shown on Table 9 the 13X and Y52 samples used in this work have formulas very near the theoretical.

The topology of faujasite and its related X and Y zeolites is the result of linking sodalite units with hexagonal prisms (see Figures 2 and 3). Each sodalite unit is linked to four other units in the previously mentioned tetrahedral configuration via hexagonal prisms which are attached to four of the eight hexagonal faces. The other four hexagonal faces and the six 4-rings are unshared. The framework of faujasite is very open and encloses a system of large cages linked by four windows of 12-rings to adjacent pores. Each cage is bounded by eighteen 4-rings, four 6-rings and four 12-rings.

The locations of various sites within the lattice are seen by focussing on one unit (Figure 3). One is looking down one of the four three-fold axes of a cubic system and seeing the other three. All the coordination sites are located on the three-fold axes and thus the ligands will be taken in sets of three. The metal ion sites are all octahedral in D_{3d} . The axes have an origin at the centre of the supercage.

One sees that the obvious first choices for cations that prefer octahedral bonding are the centres of the 16 hexagonal prisms (Site I). The octahedron is quantized here in its three-fold axis. The Si/Al is found at the corners of the edges, the oxygen near the centres of the edges. The result of occupation of Site I is the inward pull of O(3) (yielding a near octahedral co-ordination) while the six O(2) move away.

FIG. 2 The structure of faujasite, showing the aluminosilicate framework: silicon or aluminium atoms are at the apices of the truncated octahedra. (Wells (1962))

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Figure 3 Idealized projection and section through a sodalite unit of faujasite. Top: T sites lie at the intersections of the polyhedral edges. Oxygens, labeled 1 through 4, lie near the mid-points of the edges but displaced to give a tetrahedron around each T site. Four axes of inverse three-fold symmetry pass through the hexagonal prisms (one hidden) to the center (site U) of the truncated octahedron (sodalite unit), but one is hidden because it passes vertically downwards. Bottom: this is a section through abcde-jghij in top diagram showing the labeling of oxygens (1-4) and of cation sites (Roman symbols). The dashed lines show principal cation-oxygen bonds when I or I' sites are occupied; note that some of these are out of the plane of the section (Ref. 17)

Site I' provides one-sided co-ordination to three O(3) of a 6-ring of the hexagonal prism and is adjacent to Site I. It is aligned under the centre of the face of the bridging 4-ring. Although simultaneous occupancy of two I' sites of the same prism is electrostatically reasonable (17), the simultaneous occupancy of adjacent Site I and I' is rather unlikely. The above arrangement provides 16-fold Site I and 32-fold Site I'.

Each sodalite unit contains four more 6-rings, each with access to the supercage. Here there are 32-fold sites labelled II' or II according to whether displacement occurs into the sodalite unit or into the supercage. Site II' is behind the hexagonal window inside the sodalite unit and in projection is directly under the 6-edge where the two 6-faces join. Site II is opposite Site II' and in the supercage, directly under the centre of the free 6-ring. All of these sites lie on the diagonals of the cube of the unit cell, which are three-fold axes. The ions show preference for these sites as a result of coulombic forces and co-ordination preferences. For this 6-ring, three O(2) are pulled inwards to provide bonding to cations. In hydrated faujasite, electron density occurs at II, too far for simple bonding to O(2). Anions in certain partly dehydrated zeolites may lie in Site II' or I' or at Site II of the sodalite unit.

The supercage (Figure 3) is formed of sixteen 12-rings. These rings are too large for unhydrated cations, but Site V, at or near the centre, is occupied by certain hydration complexes. Due to complex X-ray data, the term Site III is used for all positions near the supercage wall (20,21). These are in front of the tetragonal window of the sodalite unit and inside the supercage, under the bridging 4-ring. Site IV defines sites too far inside the supercage to permit simple bonding to framework oxygens. It is on the four-fold axis of the cube which is not a diagonal.

The site populations as shown in Tables 2 and 3 are mathematical approximations used to fit the observed electron densities.¹ It is unfortunate that Na is only slightly denser than water. This makes it difficult for X-ray crystallographers to find enough electron density in the supercage to explain the expected number of cations and water molecules. One theory (16) concludes that "most of the water molecules and exchangeable cations in faujasite float freely through the aluminosilicate framework." Another preferred model involves preferred positions which are occupied on a temporary basis.

¹ The greater the electron density of a cation the greater the chance of distinguishing it from a water molecule. It must be noted that these electron densities are obtained from X-ray crystallography. In zeolites the broadening of electron density peaks is composed of thermal vibration and static displacements of the centres of vibration. It is very difficult to distinguish experimentally between reduction of an electron density peak by a lower occupancy factor or by a combination of thermal and static positional displacement. It is especially difficult to determine space group symmetry by X-rays.

Site I is apparently occupied by cations in several varieties. There is too much electron density at I', II' and II in some structures to allow for the maximum possible concentration of 32 water molecules per site. Therefore cations must occur in these sites but not necessarily at full occupancy. Ion exchange data (17) also indicate occupancy of sites inside the sodalite cages. As will be discussed later, there are also arguments for "mixed occupancy".

The positions of the hydroxyls in the framework are of great interest. The literature is confusing because of the numerous theories with respect to the location of the hydroxyls - an important point since most of the information available was obtained from infrared absorption spectra. Many of the proposed models are not especially plausible from a crystal-chemical point of view.

One finds in the literature (22) a single crystal X-ray study of H-faujasite which clarifies the locations of the framework hydroxyls. The model (Figure 3) places H(1) projecting into the supercage from O(1) of the wall of a hexagonal prism and H(2) projecting from O(3) in the plane of the shared 6-ring. Approximately one-sixth of the framework oxygens must be hydroxyls, which corresponds to one-third of O(1) and O(3) in this model. The infrared peaks have comparable intensities although the 3550 cm^{-1} peak has a greater area which suggests that the H(2) population is greater.²

² The longer T-O(3) distance also suggests a larger population of H(2) than of H(1); however T-O bond lengths can vary merely from linkage-related effects.

TABLE 4 Zeolite Infrared Assignments, cm^{-1}

Hydroxyls

Hydroxyl stretching modes	3800 - 3000
Water bending bands	1700 - 1600
Hydroxyl at external surface or occluded silica residue	3750 - 3740
Framework hydroxyl projecting into supercage	3650
Framework hydroxyl projecting into sodalite-prism	3550

Mid infrared

Asymmetric Si-O and Al-O stretching in tetrahedra (vibs.)	950 - 1050
Al-O vibration	568, 610, 760
Chain frequency of alternating SiO_4 and AlO_4	630 - 545
Symmetric Si-O-Si stretching modes	1140
Si-O-Si and Si-O-Al asymmetric stretching	1000
Si-O-Si out of plane bending mode	505
Bending modes	800 - 350
Si-O bond	800 - 770
Al-O vibration	780 - 680
Deformation vibrations of Si-O in SiO_4 tetrahedra	460 - 440

In general the spectra tend to be simple, with relatively few main vibrations, resembling the infrared spectra of silicate glasses. This indicates a high degree of lattice coupling of the tetrahedral vibrations in the framework. It has also been suggested (27) that the broad bands or the observed absorption profiles for zeolite framework vibrations in the infrared are an envelope of unresolved vibrations of SiO_4 and AlO_4 tetrahedra.

^aTABLE 13 Assignment of Cations (and Residual Oxygen Species) in Dehydrated Faujasite-type Zeolites ^d

Specimen ^b	X-Ray ^c Technique	Site Population				Heat Treatment, °C; Comments	Reference
		I	I'	U	II'		
Na-faujasite	sc	10 Na	9 Na		32 Na	350; vacuo	Dodge (94)
Na-faujasite	sc	9.3 Na	16.7 Na		31 Na	420; vacuo	Hsue (78)
K-faujasite	sc	8.6 K	12.9 K		32 K	400; vacuo	Pluth (92)
Ca-faujasite	sc	14.2 Ca	2.6 Ca		11.4 Ca	475; vacuo	Bennett and Smith (95)
Ni ₂ Na ₂ -faujasite	sc	10.6 Ni	3.2 Ni		6.4 Ni	400; vacuo	Olson (96)
			5.8 O _x	1.9 Ni			
				1.9 O _x			
Ba-faujasite	sc	7.3 Ba	5.0 Ba		11.3 Ba	500; vacuo	Pluth (92)
La-faujasite	sc	11.8 La	2.5 La		1.5 La	475; vacuo (data at RT)	Bennett and Smith (93)
La-faujasite	sc	11.7 La	2.5 La		1.4 La	475; vacuo (data at 420°C)	Bennett and Smith (97)
Ce, etc.-faujasite	sc	3.1 La	11.5 Ce		10.7 Na	350; vacuo	Olson <i>et al.</i> (95)
Natural faujasite	sc	12.8 Ca			10.4 Ca	420; vacuo	Hsue (78)
Na-Y(57)	p	7.8 Na	20.2 Na		31.2 Na	350; vacuo	Eulenberger <i>et al.</i> (98)
Na ₂ H ₂ Y	p	7 Na	7 Na		13 Na	400; vacuo	Gallezot and Imelik (99)
Na ₂ H ₂ Y	p	1 Na	3 Na		10 Na	400; vacuo	Gallezot and Imelik (99)
Na ₂ H ₂ Y	p	2 Na	3 Na		4 Na	300; vacuo	Mortier <i>et al.</i> (81)
K-Y(18)	p	6.4 K	14 K		26 K	300; vacuo	Mortier <i>et al.</i> (81)
K-Y(55)	p	5.4 K	18 K		27 K	300; vacuo	Eulenberger <i>et al.</i> (98)
K-Y(57)	p	12.0 K	11 K		30 K	350; vacuo	Eulenberger <i>et al.</i> (98)
Ag-Y(57)	p	16 Ag	11 Ag		28 Ag	350; vacuo	Smith <i>et al.</i> (100)
La ₂ Na ₂ Y	p	13 O _x	16 La	3 O _x	29 O _x	725; vacuo (data at 725°C)	Smith <i>et al.</i> (100)
La ₂ Na ₂ Y	p	5.2 La	8.9 La		5.5 La	380; vacuo	Gallezot and Imelik (101)
Ce ₂ Na ₂ H ₂ Y	p	5.8 Ce	1.9 Ce		10 Na	380; ambient	Gallezot and Imelik (101)
Ce ₂ Na ₂ H ₂ Y	p	1.5 Ce	8.3 Ce		7 Na	600 (also data for 200°C)	Gallezot and Imelik (102)
Ni ₂ Na ₂ Y	p	11.3 Ni	1.9 Ni		20 Na	600 (also data for 140-300°C)	Gallezot and Imelik (102)
Ni ₂ Na ₂ Y	p	11.7 Ni	1.1 Ni		21 Na	600 (also data for 200°C)	Gallezot and Imelik (102)
Ni ₂ Na ₂ Y	p	8.8 Ni	1.7 Ni		27 Na	500; vacuo	Gallezot <i>et al.</i> (103)
Cu ₂ Na ₂ Y	p	3.2 Cu	11.1 Cu		20 Na	300; vacuo	Gallezot <i>et al.</i> (103)
Cu ₂ Na ₂ Y	p	1.7 Cu	9.9 Cu		8 Na	400; vacuo	Olson (104)
Cu ₂ X	p	7.5 Cu	17 Cu		17 Ca		
			9.0 Ca				
			10 O _x				
ST-X	p	11.2 Sr	7.0 Sr		19 Sr	400; vacuo	Dempsey and Olson (105)
			4.2 Sr				
ST-X	p	6.1 Sr	12.0 Sr		20 Sr	680; vacuo	Dempsey and Olson (105)
			5 O _x				
			6.4 Sr				
Na-X(81)	sc	3.1 Na	32 Na	3 O _x	32 Na	420; vacuo; 8 Na in III,	Hsue (78)
Ni ₂ (Ce ₂ X(88))	p	1.2 Ce	2.3 Ce	1 O _x		540; N ₂ (also density at V)	Hunter and Scherzer (91)
Ni ₂ (Ce ₂ X(88))	p	3.2 Ce	2.1 Ce	6 O _x		540; air	Hunter and Scherzer (91)

^b Bracketted number is Al atoms per cell.

^c Legend: sc, single crystal, p, powder

^d Data for Cu₂Y and Cu₂X dehydrated at 200°C and 600°C given by Gallezot and Imelik (106).

^d Reference 17

It has been proposed from electrostatic considerations that

- (a) each of the thirty-two 6-rings contains one H(2) lying in the plane of the ring, while 27 H(1) project into the cavity;
- (b) each H condenses with an oxygen bonded to one Al and one Si (i.e. half of the available oxygens of this type);
- (c) if Al and Si are ordered accordingly to the theoretical meta-para combination for Si, Al = 2 there would be only one type of electrostatic field for H(1) and H(2), corresponding to the observation of only two infrared bands.

However in Na, H varieties of X and Y zeolites the narrow 3650 cm^{-1} band has been assigned (23) to a proton attached O(1) while the broad 3550 cm^{-1} band has been assigned (23) to O(2), O(3) and O(4).

A further study of infrared spectra reveals more structural aspects. The mid-infrared region of $1300\text{--}200\text{ cm}^{-1}$ contains the fundamental vibrations of Si, AlO_4 units. Two types of vibrations are identified. The first is the vibration within the AlO_2 and SiO_4 tetrahedra and the second is due to vibration of oxygen bridging bonds connecting the tetrahedra. The band seen at $1050\text{--}950\text{ cm}^{-1}$ is the most intense of the first type. This is the asymmetric Si-O and Al-O stretching in the tetrahedra. Its frequency is sensitive to Si-Al ratio and is influenced by the counter ion. The band near 760 cm^{-1} is assigned to an Al-O vibration common to aluminosilicates. The bands near 758 , 610 and 568 cm^{-1} are sensitive to changes in framework Si/Al composition. With increasing Si content the intensity of the band near 568 cm^{-1} decreases and shifts to a higher frequency. The framework vibrations are sensitive to cation type and charge.

A band in the region $630-545\text{ cm}^{-1}$ has been assigned (24) to a chain frequency of alternating SiO_4 and AlO_4 tetrahedra present in the crystal lattice. This chain frequency band is characteristic of all synthetic and natural zeolites and its frequency is dependant upon both the Si/Al ratio and the crystal structure of the zeolite. A decrease in this band accompanies crystallographic decomposition.

A shoulder seen at 1150 cm^{-1} in both X and Y (although not as prominent in X) has been identified (25) as being due to the unspecified topology of the framework, somehow involved with the connections between the tetrahedra. Bands near 1140 cm^{-1} (26) have been assigned to symmetric Si-O-Si stretching modes; 1075 cm^{-1} to a symmetric Si-O-Al stretching mode; the strongest band near 1000 cm^{-1} (not seen) to both Si-O-Si and Si-O-Al assymetric stretching modes which, because of strong coupling of adjacent groups results in an averaging effect rather than discrete bands. The shoulder near 505 cm^{-1} (found in NaY but not NaX zeolites) is assigned to an Si-O-Si out of plane bending mode. The remainder of the bands in the region of 800 cm^{-1} to 350 cm^{-1} are attributed to various more or less strongly coupled bending modes.

Further work (24) assigned a band near $800-770\text{ cm}^{-1}$ (seen at 775 cm^{-1}) to an Si-O bond and the bands in the region $780-680\text{ cm}^{-1}$ to an Al-O vibration. The bands in the $640-540\text{ cm}^{-1}$ region are assigned to chainlets of tetrahedra in the Si, Al-O skeleton following the chain frequency mentioned above. Vibrations near $460 - 440\text{ cm}^{-1}$ are assigned to deformation vibrations of Si-O bonds in the SiO_4 tetrahedron. All of the above infrared assignments are summarized in Table 4.

TABLE 4 Zeolite Infrared Assignments, cm^{-1}

Hydroxyls

Hydroxyl stretching modes	3800 - 3000
Water bending bands	1700 - 1600
Hydroxyl at external surface or occluded silica residue	3750 - 3740
Framework hydroxyl projecting into supercage	3650
Framework hydroxyl projecting into sodalite-prism	3550

Mid infrared

Asymmetric Si-O and Al-O stretching in tetrahedra (vibs.)	950 - 1050
Al-O vibration	568, 610, 760
Chain frequency of alternating SiO_4 and AlO_4	630 - 545
Symmetric Si-O-Si stretching modes	1140
Si-O-Si and Si-O-Al asymmetric stretching	1000
Si-O-Si out of plane bending mode	505
Bending modes	800 - 350
Si-O bond	800 - 770
Al-O vibration	780 - 680
Deformation vibrations of Si-O in SiO_4 tetrahedra	460 - 440

In general the spectra tend to be simple, with relatively few main vibrations, resembling the infrared spectra of silicate glasses. This indicates a high degree of lattice coupling of the tetrahedral vibrations in the framework. It has also been suggested (27) that the broad bands or the observed absorption profiles for zeolite framework vibrations in the infrared are an envelope of unresolved vibrations of SiO_4 and AlO_4 tetrahedra.

Cation Exchanged Zeolites

A metal ion commonly exchanged onto zeolites is chromium, due mainly to the ease of reduction. However there has been a good deal of uncertainty of which oxidation states of chromium actually exist, with every oxidation state from II to V having been proposed (2, 28-32).

The uncertainty arises from the complexity of systems containing ionic chromium at a solid interface since not only are there several oxidation states available but a number of chromium complexes may be stabilized on solid surfaces (4, 33, 34).

The current model (2-5) has been that a major fraction of Cr(III) (introduced via aqueous ion exchange with the $[\text{Cr}(\text{H}_2\text{O})]^{3+}$ complex cation) is reduced to the divalent state by either of the following simplified mechanisms (35, 36).

Evidence in support of this model has been provided by a variety of methods, including diffuse reflectance spectroscopy, analysis of gases over the samples, as well as EPR and infrared spectra after adsorption of probe molecules such as CO or NO.

However there has also been evidence provided to show that reduction of Cr(III) does not occur to any great extent upon dehydration; that EPR and IR parameters of nitrosyl complexes formed upon addition of nitric oxide to the dehydrated Cr-zeolite may be better explained on the basis of a Cr(III) precursor (1).

It is this second step which has been questioned since its possibility first arose (37). It was also noticed throughout the long debate over the cyclic or non-cyclic nature of the mechanism that not one study had examined whether the end product of the cycle was indeed the same as the initial product. To this end Differential Thermal Analysis (DTA), Thermogravimetric Analysis (TGA) and magnetic susceptibility theory were applied and from this came the rather startling revelation that the two were in fact not at all identical. Literature searches revealed that among the vast amount of data on zeolitic structure and yield estimates of the electrostatic field gradients there was no definitive interpretation of the structure of exchanged zeolites. The various electrostatic bonding models have been used as guides, however the simplest models interpret the experimental data on the basis of local electrostatic effects while the more complex models sum together the electrostatic contributions from the entire crystal. These models are considered fairly realistic for many exchangeable cations but are inadequate for cations with strong directional bonding such as those of the first group of transition metals (17) i.e. the cations exchanged in this work.

Hence this work became a study of not only the redox mechanism but also the structure of the exchanged zeolites.

Dehydration of Zeolites

Dehydration of a zeolite is a complex process involving adjustments between all the structural components and the external environment.

For the faujasite family, most water is lost by about 400°C (12) but strongly polarizing cations hold the last water tenaciously. Thermal breakdown for Na-X is near 760°C, for Na-Y is between 760-800°C and for ultrastable varieties is over 1000°C. In general, greater stability accompanies an increase of the Si/Al ratio. While rare earth cations augment the stability of X and Y, probably because of formation of a complex inside the sodalite cage, Ca and Sr reduce the stability.

There has developed from submicroscopic evidence a model of dehydration (12);

- (1) At low temperature under high humidity, the aluminosilicate framework adopts a relaxed configuration as the cations and water molecules assume positions consistent with chemical equilibrium. Water molecules exchange frequently from one site to another, but the framework gives an overall crystallographic control which distinguishes zeolitic water from amorphous liquid water.
- (2) With increasing temperature and decreasing humidity, water molecules escape. For weakly polarizing cations, there appear to be no major complications. As dehydration proceeds, that cations move towards framework oxygens. The water molecules no longer smooth out the electrostatic fields, and the alumino-silicate framework goes into a tensed configuration governed by both topological and chemical factors. In the zeolites containing sodalite units the tensed configuration involves local twists. Cations affect the shape of the tensed framework by adopting different sites and by pulling framework oxygens to the required bond distances. The lumpy nature of thermogravimetric (TGA) curves probably results from the formation of a series of intermediate structures.

- (3) For strongly polarized cations, major complications occur. Polarization of a water molecule yields a hydroxyl bonded to the cation plus a proton which attaches itself to a framework oxygen. Transition metal cations bond to three oxygens for a 6-ring and a hydroxyl. Ultimately as the temperature increases, the hydroxyls are destroyed with the expulsion of water.
- (4) No simple rules can be given for the thermal stability of a zeolite. Large pore frameworks should tend to be less stable because of weaker long-range interactions, but the effects of the Si-O-Si angle on the contribution from covalent bonding have not been investigated. Such large-pore frameworks might be highly persistent because of the high activation energy for breaking Si-O bonds. The actual reaction velocity should depend greatly on the presence of defects. Entrance of Al causes further complications since the chemical nature of the compensating cation is another variable. The experimental data show a tendency for the thermal stability to decrease as the Al/Si ratio increases but the idiosyncratic effect of cations confuses the pattern. Breakage of an Al-O bond should require less activation energy than of an Si-O bond. There is no scientific understanding of the topologic effect on stability.
- (5) A definite distinction must be made between simple thermal stability and stability in a complex chemical system. Traces of water probably act as catalysts for hydrothermal degradation. Numerous data on silicates testify to enormous increases of reaction velocities in the presence of water.

EXPERIMENTAL

Materials

Zeolites were obtained from Union Carbide Corporation Linde Division. They were Linde 13X lot 13945030049 and 8876 Linde LZ-Y52 lot 020580 (formerly known as SK40). Both were powder samples. Before being used they were washed free of sodium silicates. Chemicals used were all reagent grade, spectral grade whenever available. Water used throughout was doubly distilled and freshly deionized.

Instruments

Atomic absorption was run by Dr. Stephen Lee of the Analytical Laboratory of Carleton University on the instrument AA-5000 with HGA-500 (P.E.). Operation condition was AA-BG balanced.

Purge gas:	Ar
Wavelength:	Cr 337.8 nm
	Fe 284.2 nm
	Al 309.2 nm
SBW:	Cr 0.7 nm
	Fe 0.2 nm
	Al 0.7 nm

Heating program is shown later in the appropriate section (Table 7).

Attention was then turned to multiple exchanges. Again two difficulties arose. It was impossible to remove the filtrate from the first exchange without going through the entire procedure with centrifugation and then returning the exchanged zeolite to the flask. This only added opportunities for oxidation. Secondly, whereas there had been no difficulty with the pH of the Cr(III) exchange, there most certainly was with the Cr(II) exchange. Upon the second exchange the pH dropped considerably and the zeolite gelled out, i.e. complete lattice destruction.

It was obviously necessary to find a buffering system which would retain an appropriate pH level without itself interfering with the exchange, i.e.

- (1) a large enough cation that would not itself enter the cage and preferentially exchange onto the lattice (i.e. must exceed the Van der Waal's dimension of $13\text{\AA}$ for 13X and $52\text{\AA}$ for Y52);
- (2) one which would function within the correct pH range and
- (3) most importantly, would not oxidize the Cr(II) already in place, as well as
- (4) not destroying the lattice itself.

Repeated efforts to form such a buffer were to no avail and multiply Cr(II) exchanged zeolites were not obtained.

Sample Notation

Samples were prepared and labelled in the following manner.

$$N - M^{n+} (Z)^E TD$$

where	N - number of sample	i.e.	2
	M - metal ion exchanged onto zeolite	i.e.	Cr
	n - oxidation state of M	i.e.	3 ⁺
	Z - zeolite	i.e.	13X
	E - number of times exchanged	i.e.	4
	T - temperature at which dehydration occurred, if any	i.e.	110°C
	D - drying technique used		

where VD - vacuum dried

OD - oven dried

AD - air dried

C - centrifuged

Preparation of Exchanged Zeolite

Samples were prepared as shown in Tables 2 and 3 for Cr(III) and Fe(III). Zeolites 13X and Y52 were wetted in 25 ml H₂O. Ion to be exchanged was placed in 300 ml H₂O. Amounts of ion to be exchanged were prepared to be either 0.02 moles or 8.75 x 10⁻³ moles. Solutions were stirred with teflon coated magnetic stirrers and were protected from photochemical reactions. The pH of the solution was noted, and if necessary raised with 6N NH₄OH to within the pH 5-6 range in order to maintain the zeolite framework.

TABLE 5 - Preparation Chromium Exchanged Zeolites 13X and Y52

Sample	Amount Zeolite ±.01g	Amount ^a Exchanged Cr(NO) ₃ ·9H ₂ O	pH ⁱⁿ	Time still (hr)	Time settle	Filter whatman #	Colour filtrate	Colour zeolite	pH fil.	Air dry (d)	Yield (g)
1-Cr ³⁺ (13X) ¹ AD	25.00	8.00103	5.0	4	4	42	clear colourless	gray green	5.5	2	
2-Cr ³⁺ (13X) ¹ AD	25.03	8.00196	5.0	4	4	42	same	same	5.5	2	
1-Cr ³⁺ (13X) ⁴ AD	25.00	7.9536	5.5	3	4	41	same	same	5.5		
		7.9638	5.5	3	4	41	clear green	same	5.5		
		3.4800	5.5	3	4	41	same	same	5.5		
		3.5209	5.5	2	4	41	same	same	5.5	2	29.133
2-Cr ³⁺ (13X) ⁴ AD	25.0099	7.9974	5.5	2	4	41	same	same	5.5		
		0.0009	5.5	2	4	41	same	same	5.5		
		3.5009	5.5	2	4	41	same	same	5.5		
		3.5382	5.5	2	4	41	same	same	5.5	2	28.737
3-Cr ³⁺ (13X) ⁴ AD	25.0271	8.0000	5.5	2	4	41	same	same	5.5		
		7.9993	5.5	2	4	41	same	same	5.5		
		3.5047	5.5	2	4	41	same	same	5.5		
		3.5000	5.5	2	4	41	same	same	5.5	2	
4-Cr ³⁺ (13X) ⁴ AD	25.0077	8.0088	5.5	2	4	41	same	same	5.5		
		8.0000	5.5	2	4	41	same	same	5.5		
		3.4991	5.5	2	4	41	same	same	5.5		
		3.4995	5.5	2	4	41	same	same	5.5	2	
1-Cr ³⁺ (Y52) ¹ AD	10.0000	8.00453	4.0	3	3	42	blue	blue	4.5	2	
2-Cr ³⁺ (Y52) ¹ AD	10.0000	4.00443	4.0	3	3	42	blue	blue	4.5	2	

^a grams ± 0.0001 of 0.00001 as appropriate

TABLE 6 - Preparation Iron Exchanged Zeolites 13X and Y52

Sample	Amount Zeolite $\pm 0.1g$	Amount ^a Exchanged $Fe_2(SO_4)_3 \cdot xH_2O$	pH sol'n	Time stir (h)	time settle (hr)	Filter Whatman #	Colour filtrate	Colour zeolite	pH ^b fil	Air dry (d)	Yield (g)
1-Fe ³⁺ (13X) ⁴ AD	25.0091	5.6226	5.5	3	3	41	clear	gold	5.5		
		5.6214	4.0*	3	3	41	same	gold	5.5		
		2.4588	4.0*	3	3	41	same	gold	5.5		
		2.4588	4.0*	3	3	41	sl. yellow	gold	5.5	6	
2-Fe ³⁺ (13X) ⁴ AD	25.0086	5.6218	5.5	3	3	41	clear	gold	5.5		
		5.6210	4.0*	3	3	41	same	gold	5.5		
		2.4588	4.0*	3	3	41	same	gold	5.5		
		2.4588	4.0*	3	3	41	sl. yellow	gold	5.5	6	
1-Fe ³⁺ (13X) ⁷ AD	25.0038	5.6233	5.5	3	3	41	clear	gold	5.5		
		5.6215	4.0*	3	3	41	same	gold	5.5		
		5.6209	4.0*	3	3	41	same	gold	5.5		
		5.6200	4.0*	3	3	41	sl. yellow	gold	5.5		
		5.6209	4.0*	3	3	41	same	gold	5.5		
		5.6250	4.0*	3	3	41	same	gold	5.5		
		5.6243	4.0*	3	3	41	same	gold	5.5	6	
2-Fe ³⁺ (13X) ⁷ AD	25.0056	5.6219	5.5	3	3	41	clear	gold	5.5		
		5.6209	4.0*	3	3	41	same	gold	5.5		
		5.6228	4.0*	3	3	41	same	gold	5.5		
		5.6221	4.0*	3	3	41	sl. yellow	gold	5.5		
		5.6208	4.0*	3	3	41	same	gold	5.5		
		5.6208	4.0*	3	3	42	same	gold	5.5		
		5.6208	4.0*	3	3	42	same	gold	5.5	6	
1-Fe ³⁺ (Y52) ¹ AD		5.6208	4.0*	3	3	42	same	gold	5.5		
1-Fe ³⁺ (Y52) ¹ AD	10.00	2.81852	3.0	5	2	42	clear	gold	4.5		
2-Fe ³⁺ (Y52) ¹ AD	10.00	5.61980	<	5	2	42	clear	gold	4.0		

*raised to pH 5.5 of 6.0

b - diluted to 500 ml

a - ± 0.0001 or 0.00001 as appropriate

Accidental destruction of the zeolitic frame was a major concern during the exchange of transition metals onto molecular sieves. Destruction can occur in two circumstances, one the maintenance of an inappropriate pH range (appropriate being 4.5 to 6) and the second the forcible exchange of too many metal ions onto the lattice.

There is a secondary concern regarding the pH of the exchanging solution. It is known that at a pH of 4, Fe(III) enters the zeolitic structure as $\text{Fe}(\text{OH})^{2+}$ (38).

Studies have shown that structure and crystallinity are destroyed at high levels of exchange for NaX (39). Loss of crystallinity begins at 15 to 23% exchange, but one can retain the zeolitic structure up to 30% for 13X if the exchange takes place at room temperature and a pH of less than 4. At 50% exchange one sees a loss which may be dependent on both temperature and pH.

As this work dealt with powder samples there was no anxiety over a loss of crystallinity. The results in Table 9 show exchange rates from 18 to 78%, of which four were over 30% and two over 50%. The framework structure of the samples was monitored by X-ray diffraction. It is known that in powder samples many X-ray intensities are lost in the background or are confused by overlapping diffraction lines (17). The results indicated the Fe^{3+} (13X)⁷AD sample, 78.70% exchanged, had suffered a change in zeolite structure. The other samples remained intact. Previous studies have shown exchange levels of only 6 Cr per zeolitic unit (40), yet this study has successfully exchanged 8.1 Cr(III) on Y52, 10.4 Cr(III) on 13X and 6.3 Cr(II) on 13X as well as 16 Fe(III) on Y52 and 14.0 Fe(III) on 13X, each per unit cell and with no breakdown of the cell structure, whereas only 7 Fe(III) had been expected (40).

It is interesting to note that in every case, all of the chromium of the first exchange was in fact placed onto the lattice (as is evidenced by the colourless filtrate, refer to Table 5); and although the second filtrate (green) indicated that not all of the chromium made available to the lattice was exchanged, it was possible to place more chromium onto the frame in further exchanges. This was proven by analysis of the filtrates, which showed high enough levels of sodium and significantly decreased levels of chromium. The same held true for the iron exchanges. The resulting lattice structure is discussed in terms of thermal, spectroscopic and magnetic evidence below.

Preparation of $1\text{-Cr}^{2+}(13\text{X})^1\text{C}$

Note that great care must be taken with this procedure. Apparatus was set-up as in Figure 4 and evacuated. Mossy zinc (40 mg) and 8g $\text{K}_2\text{Cr}_2\text{O}_7$ (0.027 mol) were placed dry in a suction flask. Water (50 ml) was placed in the beaker covering the end of the siphon. Concentrated HCl (115 ml) was added to 60 ml water and placed in the upper dropping funnel. The acid was added to the solids slowly until a vigorous evolution of hydrogen occurred. The acid was then added quickly enough to maintain the reaction until the solution became a pure blue colour. While hydrogen was still evolving the rubber tubing to the siphon was pinched to force the solution into the lower dropping funnel where it was isolated. The 25 g of zeolite wetted with 50 ml water was already in place in the round bottom flask and was purged with N_2 gas. The solution was stirred constantly. The Cr(II) solution was added and stirred for four hours. The colour of the drops in the funnel above indicated the state of the chromium, in this case still in its Cr(II) oxidation state.

FIGURE 4
Apparatus for Exchange of Chromium (II)

The flask was then sealed under N_2 and transferred to a glove bag where the solution was transferred to four centrifuge tubes which were sealed under nitrogen. The tubes were centrifuged for 20 minutes at 10K. Separation occurred neatly. The filtrates were clear, although two of the four tubes had an oxidized filtrate, indicated by its green colour, while two had an unoxidized filtrate (still pure blue). All the filtrates were transferred under nitrogen to volumetric flasks and were diluted to 500 ml. The zeolites were retained in the sealed centrifuge tubes and stored in the dark. Colour indicated that they were still Cr(II) and were successfully stored as such.

Preparation of $2-Cr^{2+}(13X)^2C$

As above, with 25.0081 g or 13X, 40 g mossy zinc and 8 g $K_2Cr_2O_7$ and 80 ml concentrated HCl with 40 ml water. Stirred for four hours. Centrifuged for 20 minutes at 10K. Total filtrate was transferred to 500 ml volumetric flask where it oxidized immediately. Transferred the exchanged 13X to the reaction flask and repeated as above with 8g of $K_2Cr_2O_7$, 40 g mossy zinc, 120 ml of the acid solution, stirred for three hours and centrifuged. The second filtrate was decanted into a 500 ml volumetric. Whereas the first filtrate had a pH of 5.1, this second filtrate had a pH of 3.5 and it had gelled out. The zeolitic framework had been destroyed.

This Cr(II) exchange is considered to be quite difficult. Although obtaining a Cr(II) solution is a standard procedure, the isolation of it for long enough to do something with it is not common. However, its colour (bright blue) enables ease of monitoring and once the system for exchange was linked to the generation equipment (Figure 4) the product was easily obtained.

However, further manipulation proved exceedingly difficult. Attempts to decant the solution from the zeolite after settling proved fruitless even when conducted within a glove bag or box. Filtration was impractical due to the increased time needed and therefore greater opportunities for oxidation. It was noted that the Cr(II) solution oxidized extremely quickly while the zeolite did not show much evidence of change in colour in the same circumstances, although it did when outrightly exposed to the atmosphere. This leads to two possibilities - one that Cr(II) on the lattice is a good deal more stable than anticipated, the other that although oxidation did take place there was no longer a corresponding colour change to indicate the reaction. For this reason it was decided to store samples with a small amount of solution and use the solution as an indicator.

A method was devised for separation of the zeolite from the majority of the solution. After exchange the solution was not allowed to settle. Instead the round bottom flask was sealed under N_2 and placed within a nitrogen purged triply lined glove bag which was then placed within a glove box purged with nitrogen gas obtained from a dewar of liquid nitrogen. There the solution was quickly transferred to sealable centrifuge tubes and removed for centrifugation. The state of the solutions - which remained bright blue in most cases - indicated the durability of the seal. After centrifugation the majority of the solution was decanted and the remaining zeolite was stored within the sealed tubes with a small amount of solution to act as an indicator. This method worked satisfactorily and the solution and zeolite could be thus stored safely for long periods of time, away from light.

Attention was then turned to multiple exchanges. Again two difficulties arose. It was impossible to remove the filtrate from the first exchange without going through the entire procedure with centrifugation and then returning the exchanged zeolite to the flask. This only added opportunities for oxidation. Secondly, whereas there had been no difficulty with the pH of the Cr(III) exchange, there most certainly was with the Cr(II) exchange. Upon the second exchange the pH dropped considerably and the zeolite gelled out, i.e. complete lattice destruction.

It was obviously necessary to find a buffering system which would retain an appropriate pH level without itself interfering with the exchange, i.e.

- (1) a large enough cation that would not itself enter the cage and preferentially exchange onto the lattice (i.e. must exceed the Van der Waal's dimension of $13\text{\AA}$ for 13X and $52\text{\AA}$ for Y52);
- (2) one which would function within the correct pH range and
- (3) most importantly, would not oxidize the Cr(II) already in place, as well as
- (4) not destroying the lattice itself.

Repeated efforts to form such a buffer were to no avail and multiply Cr(II) exchanged zeolites were not obtained.

Dehydration of Exchanged Zeolites

Samples in the area of 1 g were dehydrated to temperatures of 110, 120, 150, 200 and 250 °C. All samples were dehydrated on a vacuum line with a ground pump and mercury diffusion pump. Samples were placed on the line in a sand bath whose temperature was controlled by a transformer and monitored by a thermometer placed in the sand at a depth equivalent to that of the sample. Samples were protected from the light and evacuated with heating up to as long as 60 hours with continual evacuation. Samples were then cooled to room temperature (24°C) over a 24 hour period under vacuum but with no further pumping. They were then transferred under nitrogen into sealed tubes.

Samples were maintained sealed under nitrogen as there were questions to be asked with respect to their stability in terms of

- (1) oxygenation - stability of Cr(II) formed;
- (2) rehydration;
- (3) thermodynamics;
- (4) irreversibility of dehydration.

As the samples were heated under vacuum, the colour changed from green to gray and from gold to yellow for chromium and iron respectively.

Rehydration of Exchanged Zeolites

Samples were weighed out under nitrogen and immersed in 20 ml water for 48 hours, being warmed to ~50°C. They were then filtered with tared Whatman #42 filter paper and air dried under cover.

Digestion of Exchanged Zeolites

Samples of ~0.5 g were placed in teflon cups with 5 ml concentrated HF, 5 ml concentrated HNO_3 and 3 ml H_2SO_4 and heated to dryness. The product was then dissolved in 25 ml H_2O and 2.5 ml concentrated HF at low heat and with stirring. Samples digested were all those exchanged, dehydrated and the unexchanged 13X and Y52. Sample sizes are shown with the analytical results in Table 8.

Preparation of Reagents for Sodium Analysis

Dissolved 18.0 g uranium acetate in 12 ml glacial acetic acid and 200 ml water. Heated at 70°C until clear. Dissolved 111.0 g magnesium acetate in 12 ml glacial acetic acid and 200 ml water. Heated at 70°C , until clear. The two solutions were then mixed at 70°C and stirred. They were then cooled to 20°C and after filtering, were stored away from light.

The washing solution was prepared by saturating 400 ml of 95% EtOH with the above reagent, filtering and storing away from light. Details may be found in reference 41.

Sodium Analysis

Samples of digested zeolite (0.5 or 1.0 ml) were added to 15 ml of the reagent. The solution was stirred vigorously for 30 minutes, filtered through fine glass crucibles which had been previously heated at 70°C for thirty minutes and then tared, and heated at 70°C for 30 minutes and weighed as $\text{NaMg}(\text{UO}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 6.5 \text{H}_2\text{O}$. Results are seen in Table 8. Errors represent the sum of percentage error from the weight of the exchanged zeolite sample and the percentage error found in the sodium determination. Each sample was run in triplicate.

Atomic Absorption Analysis

Analysis was performed by Dr. Stephen Lee of the Analytical Laboratory of Carleton University. Digested samples were used for the analysis. Results are shown in Table 8, with the heating program shown in Table 7. Errors represent the sum of the percentage error from the weight of the exchanged zeolite and percentage errors obtained from standard deviation of atomic absorption results.

Molecular Formula's and Weights

Molecular formulas were calculated from the analytical results and using the ratio $\text{Si} + \text{Al} = 192$ and $\text{O}_2 = 192$. The final error is carried over from the aluminum. Water content was determined from thermogravimetric data. Errors were taken as the readable limits of the chart paper. Results are shown in Tables 8 and 9, as are the Al/Si ratios.

Percentage Exchange

Percentage exchange is calculated using the formula (39)

$$\% \text{ Exchange} = \frac{100 \ a \ M_2}{86/a \ M_1}$$

where a - actual weight of ion per gram of zeolite

M_1 - molecular weight of the exchanged cation

M_2 - molecular weight of the exchanged zeolite (from Table 9)

e - oxidation state of the exchanging cation

Results are shown in Table 9.

TABLE # Atomic Absorption Heating Modes

Element	Setting/Step	Temp °C	Ramp/s.	Hold/s.	Gas Flow Rate mL/min.
Cr	Dry	130	5	15	300
	Charring	900	5	20	300
	Atomization	2700	1	6	50
Fe	Dry	130	5	15	300
	Charring	1000	5	20	300
	Atomization	2600	1	6	10
Al	Dry	130	5	15	300
	Charring	600	5	20	300
	Atomization	2700	1	6	10

TABLE 8 Analysis Results

Sample	Amount digested (mg) ^a	Na Analysis			AA Analysis			TGA Analysis		
		mg/sample	Al	mg/sample	Fe	mg/sample	Cr	H ₂ O loss (mg) ^b	Sample size (mg) ^c	
13X	508.04	76.4 ± 0.05	85.70 ± 7.99	0.71 ± 0.11				2.85	10.90	
Y52	461.40	44.10 ± 0.01	57.84 ± 1.35	1.21 ± 0.16				2.69	10.31	
Cr ³⁺ (13X) ¹ AD	505.04	59.93 ± 0.02	85.70 ± 7.99			13.51 ± 0.03		2.92	11.10	
Cr ³⁺ (13X) ⁴ AD	326.51	28.86 ± 0.03	56.43 ± 0.19			13.43 ± 0.09		2.65	9.85	
Cr ²⁺ (13X) ¹ C	513.21	53.96 ± 0.05	88.57 ± 0.53			13.12 ± 0.13		2.37	9.09	
Cr ³⁺ (Y52) ¹ AD	501.43	27.18 ± 0.03	63.60 ± 0.96			16.70 ± 0.07		2.52	9.42	
Be ³⁺ (13X) ⁴ AD	692.62	40.32 ± 0.04	127.22 ± 0.92	41.58 ± 0.20				2.74	10.05	
Fe ³⁺ (13X) ⁷ AD	756.95	5.63 ± 0.01	134.37 ± 0.97	74.53 ± 0.08				2.89	9.86	
Fe ³⁺ (Y52) ¹ AD	760.62	8.18 ± 0.01	97.06 ± 0.84	54.22 ± 0.35				2.93	10.75	
13X(120)R								2.66	9.34	
13X(120R) ²								2.46	10.96	
Y52(120R)								2.10	10.32	
Y52(120R) ²								2.83	10.15	

^a ± 0.01^b ± 0.04^c ± 0.02

TABLE 9 Molecular Formulas, Weights and Percentages Exchanged

Sample	Molecular Formula ^a			Al/Si Ratio	Molecular Weight ^b	Percentage Exchanged ^c
13X theoretical	Na ₈₆	(AlO ₂) ₈₆	(SiO ₂) ₁₀₆	1.23	18,175.9	
Y52 theoretical	Na ₅₆	(AlO ₂) ₅₆	(SiO ₂) ₁₃₆	2.43	17,257.7	
13X	Na _{87.8}	(AlO ₂) _{84.2}	(SiO ₂) _{114.2}	1.36	18,225.0	
Y52	Na _{52.9}	(AlO ₂) _{59.1}	(SiO ₂) _{132.9}	2.25	17,164.1	
Cr ³⁺ (13X) ¹ AD	Cr _{6.9} Na _{69.1}	(AlO ₂) _{84.2}	(SiO ₂) _{107.8}	1.28	18,177.7	24.03
Cr ³⁺ (13X) ⁴ AD	Cr _{10.4} Na _{50.8}	(AlO ₂) _{84.3}	(SiO ₂) _{107.8}	1.28	17,991.1	36.29
Cr ²⁺ (13X) ¹ C	Cr _{6.5} Na _{60.3}	(AlO ₂) _{84.2}	(SiO ₂) _{107.8}	1.28	17,918.3	22.59
Cr _{14.0} (Y52) ¹ AD	Cr _{8.1} Na _{29.6}	(AlO ₂) _{59.1}	(SiO ₂) _{132.8}	2.25	17,163.4	18.61
Fe ³⁺ (13X) ⁴ AD	Fe _{14.0} Na _{32.8}	(AlO ₂) _{88.3}	(SiO ₂) _{113.1}	1.28	17,840.1	48.67
Fe ³⁺ (13X) ⁷ AD	Fe _{22.5} Na _{4.1}	(AlO ₂) _{84.1}	(SiO ₂) _{107.7}	1.28	18,100.2	70.70
Fe ³⁺ (Y52) ¹ AD	Fe _{16.0} Na _{5.9}	(AlO ₂) _{59.1}	(SiO ₂) _{132.8}	2.25	17,182.1	55.66

^a Cr ±0.4 Fe ±0.4 Na ±0.2 AlO₂ ±0.2 SiO₂ ±0.4 H₂O ±0.4^b ±0.5^c ±0.05

Thermogravimetric Analysis

Water loss was calculated from the percentage weight loss of the samples. Samples were run both entirely hydrated and partially dehydrated (i.e. at 120°C). It was found that the total percentage weight loss of the partially dehydrated samples were equivalent to the percentage weight loss as extrapolated to the appropriate temperature as read off the hydrated sample - a testament to the accuracy of the instrument.

Shown is an example of a TGA spectrum, specifically of unexchanged 13X (Figure 5, solid line) and of chromium exchanged 13X (Figure 5, dashed line).

The exchanged zeolites lose water more rapidly and continue to lose water at higher temperatures. The endothermic shift of water loss at moderate temperatures (confirmed in the DTA spectra) indicates water more loosely bound in exchanged systems.

Differential Thermal Analysis

Spectra were run of all samples; exchanged, unexchanged, dehydrated and rehydrated zeolites. All samples were run twice, once against a glass reference and once against the corresponding unexchanged zeolite where applicable. Characteristics are shown in Table 10. Also shown is an example of a DTA spectrum of unexchanged 13X (Figure 6, solid line) and of chromium exchanged 13X with the 13X background removed (Figure 6, dashed line).

Figure 5 TGA of Cr Zeolite 13X (---) and Zeolite 13X (—)

Figure 6 DTA of Cr Zeolite13X(---) and Zeolite13X(—)

TABLE 10 Differential Thermal Analysis Characteristics

Sample	Reference	Peaks	
		Endo ($^{\circ}\text{C}$)	Exo ($^{\circ}\text{C}$)
13X	Glass	50 - 150 150 - 175 175 - 300	
13X(120)	Glass	225 - 350	
13X(150)	Glass	10 - 50	
13X(200)	Glass	20 - 60 90 90 - 125	60 - 90 90 - 100 100 - 150
Y52	Glass	15 - 80 85 - 125	80 - 85
Y52(150)	Glass	15 - 55 70 - 80 80 - 110	55 - 90
Y52(200)	Glass	70 - 80 80 - 125 125 - 250	75 - 100
1-Cr ³⁺ (13X) ⁴ AD	13X	100 - 350 110 - 240	
2-Cr ³⁺ (13X) ⁴ AD	13X	100 - 375 115 - 240	
1-Cr ³⁺ (13X) ⁴ 120	13X	40 - 75 90 - 100 110 - 120	
1-Cr ³⁺ (13X) ⁴ 120	Glass	90 - 250	
1-Cr ³⁺ (13X) ⁴ 150	13X	15 - 60 75 - 150	
1-Cr ³⁺ (13X) ⁴ 150	Glass	150 - 225	
1-Cr ³⁺ (13X) ⁴ 120R	13X	25 - 65 85 - 225 240 - 290	

TABLE 10 Cont'd

Sample	Reference	Peaks	
		Endo ($^{\circ}\text{C}$)	Exo ($^{\circ}\text{C}$)
1-Cr ³⁺ (13X) ⁴ 120R	Glass	85 - 100 100 - 120 140 - 250	85
1-Cr ³⁺ (13X) ⁴ 200R	13X	10 - 65 85 - 180	
1-Cr ³⁺ (13X) ⁴ 200R	Glass	85 - 150	80
1-Cr ³⁺ (13X) ⁴ 250R	13X	80 - 250	
1-Cr ³⁺ (13X) ⁴ 250R	Glass	110 - 325	110
1-Cr ³⁺ (13X) ⁴ 120	(13X)120	200 - 310 200 - 230	75 - 100
1-Cr ³⁺ (13X) ⁴ 150	(13X)150	275 - 350	80 - 110
1-Cr ³⁺ (Y52) ¹ AD	Y52	75 - 125 125 - 200	
1-Cr ³⁺ (Y52) ¹ 200	(Y52)200	80 - 125 240 - 300 350 -	80
1-Fe ³⁺ (13X) ⁴ AD	Glass	75 - 250 100 - 150	
1-Fe ³⁺ (13X) ⁴ AD	13X	75 - 250 100 - 150	
1-Fe ³⁺ (13X) ⁴ 150	(13X)150	80 - 120 225 - 260	80
1-Fe ³⁺ (13X) ⁴ 150	Glass	75 - 125 125 - 200 200 - 300	
1-Fe ³⁺ (13X) ⁴ 120	(13X)120	75 - 110 180 - 240	50

TABLE 10 Cont'd

Sample	Reference	Peaks	
		Endo (°C)	Exo (°C)
1-Fe ³⁺ (Y52) ¹ AD	Glass	25 - 55	
		75 - 210	
		90 - 140	
1-Fe ³⁺ (Y52) ¹ AD	Y52	100 - 250	
		100 - 140	
1-Fe ³⁺ (Y52) ¹ 120	(Y52)120	70 - 100	50
		150 - 225	
1-Fe ³⁺ (Y52) ¹ 150	(Y52)150	30 - 70	70
		70 - 110	
		240 - 275	
1-Fe ³⁺ (Y52) ¹ 200	(Y52)200	70 - 110	70
		240 - 300	

Both the X and Y zeolite samples had plateaus in the 750°C range, indicating a phase transfer and therefore structural collapse. However none of the samples showed any evidence of the intense exothermic peak expected. It is reasonable to assume that the framework is unstable upon dehydration and that the exothermic process of lattice destruction occurs between 100°C and 350°C and is thus masked by the endothermic process of dehydration.

The 13X sample reveals three major areas of slow endothermic dehydration between 50 and 300°C. Upon dehydration to 120°C only the last area is seen and it is shifted up to 225 to 300°C, suggesting that the remaining water molecules are very strongly bonded. The 150 - 200°C dehydrated samples show endothermic peaks at the low temperature scale. The Y52 on the other hand shows an exothermic peak in the midst of the endothermic area. As the sample is dehydrated the endothermic area remains relatively stable but the exothermic shifts up and even splits.

When the chromium is exchanged onto 13X one sees only one large endothermic area covering the same range as the 13X, within which there is a smaller area of faster loss. Upon dehydration to 120°C there is a definite downshift, as for 13X. Upon removal of the 13X background, the effect of the chromium is resolved into three endothermic peaks within the range shown by the entire sample. Upon elimination of the background of a similarly treated (13X)120, one sees a sharp exothermic peak at 75-100°C and a large endothermic peak at 200-310°C, with the major portion at 200 to 230°C. This would again indicate that there has been an internal phase transfer (or perhaps a migration) and that the remaining water is very strongly bonded.

The pattern repeats itself for the iron exchanged samples. The general downward shift upon exchange would indicate that the Na molecules are bound to the water more strongly within the zeolite than to the chromium and iron.

The DTA spectra of rehydrated samples show a strong exothermic peak immediately previous to three areas of endo activity, which lie within the endothermic area of the original sample. After removal of the zeolitic sample background one sees two endothermic areas, each preceded by a strong exothermic peak, again indicating internal migration. There is also a further endothermic area at a higher temperature than expected. There are clearly differences between the original exchanged sample and the de- and re-hydrated samples. One sees the same pattern emerging with the 150 and 200°C samples. The same pattern also holds for the Y zeolites.

The pattern repeats itself for the iron exchanged samples. Once again the general downward shift would indicate a stronger bonding of the Na to the water within the zeolite than of the iron to the water.

X-Ray Crystallography

X-ray spectra were run at Concordia University by Dr. Peter Bird. Although the lines obtained could not be directly assigned, probably because they were powder samples and literature results are primarily for crystals, the important fact is that there is no difference between the spectra of the unexchanged 13X and Y52 zeolites and the exchanged samples, with one exception. The exception is the $\text{Fe}^{3+}(\text{13X})^7\text{AD}$ sample which had a different spectrum, indicating a breakdown of the zeolitic framework.

Magnetic Susceptibilities

The instrument was calibrated with Mohr's salt (ferrous ammonium sulphate, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$ MW 392.15, $\chi = 32.04 \times 10^{-6}$ cgs at 22°C). Samples of chromium and iron, exchanged zeolites were run at three temperatures (room, helium and nitrogen) to determine if their magnetic susceptibilities are indeed temperature independent as the literature suggests. Thereafter all samples were run at room temperature. Samples were run at four field strengths.

Field 11	- 9.2 kG
10	- 8.4 kG
9	- 7.5 kG
8	- 6.5 kG

Resulting differences in mV were corrected for the pan effects and were converted into differences in weight (mg). The results are shown in Table 11. Errors were taken to be the sums of percentage errors obtained from the initial weight, the standard deviation of the data and the calculated molecular weight.

The magnetic susceptibility data are interesting in that they yield the first clue as to why the system may not be functioning as expected. The standard value for $\mu_{\text{eff}}(\text{Cr}^{3+})$ as obtained from $\mu_{\text{eff}} = (S(S+1))^{\frac{1}{2}}$ where $S = 3/2$ is 3.87 B.M., while that for $\text{Cr}(\text{II})$ is 2.83 B.M. The results show a $\mu_{\text{eff}}(\text{Cr}^{3+})$ in the exchanged zeolites as being 2.90 B.M. as opposed to 3.87 and $\mu_{\text{eff}}(\text{Cr}^{2+})$ as 1.40 B.M. as opposed to 2.83.

TABLE 11 Magnetic Susceptibilities and Effective Moments of Exchanged Zeolites

Sample	$\chi_m' \times 10^{-6}$ cgs $\pm .0001\%$	μ_{eff}	$M^{x+}(\text{Zeo})$ B.M. $\pm .001\%$	μ_{eff}	M^{x+} B.M. * $\pm .01\%$
Cr ³⁺ (13X) ¹ AD	169,698		20.02		2.90
Cr ³⁺ (13X) ¹ 120	84,428		14.12		2.05
Cr ³⁺ (13X) ¹ 150	85,282		14.19		2.06
Cr ³⁺ (13X) ¹ 200	84,861		14.16		2.05
Cr ³⁺ (13X) ¹ 150R	95,309		15.00		2.17
Cr ³⁺ (13X) ⁴ AD	166,598		19.84		1.91
Cr ³⁺ (13X) ⁴ 120	147,178		18.65		1.79
Cr ³⁺ (13X) ⁴ 150	92,550		14.79		1.42
Cr ³⁺ (13X) ⁴ 200	132,331		17.68		1.70
Cr ³⁺ (13X) ⁴ 120R	187,717		21.06		2.02
Cr ²⁺ (13X) ¹ C	35,020		9.10		1.40
Fe ³⁺ (13X) ⁴ AD	321,978		27.58		1.97
Fe ³⁺ (13X) ⁴ 120	299,810		26.62		1.90
Fe ³⁺ (13X) ⁴ 150	276,050		25.54		1.82
Fe ³⁺ (13X) ⁷ AD	584,120		37.24		1.65
Cr ³⁺ (Y52) ¹ AD	3,400		2.84		0.35
Cr ³⁺ (Y52) ¹ 200	82,430		13.95		1.72
Fe ³⁺ (Y52) ¹ AD	13,688		5.69		0.36
Fe ³⁺ (Y52) ¹ 120	15,086		5.97		0.37
Fe ³⁺ (Y52) ¹ 150	173,176		20.23		1.26
Fe ³⁺ (Y52) ¹ 200	213,655		22.47		1.40

* μ_{eff} of the metal ion alone is obtained by dividing the μ_{eff} of the total metal ion per mole of exchanged zeolite by the no. of metal ions per unit cell as obtained from Table 5.

Magnetic susceptibility results are at first glance unusual, yet after study they correlate with the general pattern that is developing. As the TGA results show that there is virtually no change after 250°C, one would expect to see an orderly decrease from room temperature to 250°C. However not only are the initial values for μ_{eff} much closer to Cr(II) than Cr(III), the trend expected is not easily seen. In the case of the singly exchanged zeolite 13X there is a sharp decrease of μ_{eff} at 120°C, which remains steady all the way to 200°C. This relates to the dimerization theory once again. At 120°C there may be enough thermal energy to begin both reduction and dimerization of the reduced Cr(II), which will drop the magnetic moment and cause the previously mentioned gray colour.

In the case of the quadruply-exchanged 13X, there is a steady decrease in value to 150°C, then at 200°C the μ_{eff} is almost equivalent to the 120°C value. Again the overall values are much lower than expected.

The Cr(II) exchanged 13X has approximately half the expected value, again pointing towards the dimerization of the exchanged chromium.

The iron values decrease in very small increments and there are not enough results available due to the structural breakdown which occurred to warrant an explanation of the trend.

The Y52 results are reversed in the sense that the μ_{eff} are increasing instead of decreasing with increasing temperature. Here one may have to take into consideration molar properties. As the temperature increases, μ_{eff} increases due to the increasing amount of thermal energy available. It is quite possible that there simply is not enough room or the correct environment is not available for dimerization, as seen in the greener Y52 than 13X.

Infrared

Infrared spectra, of which two are shown for zeolite 13X (Figure 7, solid line) and chromium exchanged 13X (Figure 7, dashed line), were run as nujol mulls. The low resolution spectra shown have areas blocked out which were examined in high resolution. Table 12 lists spectral characteristics of all samples that were used.

As seen in the spectra, the hydroxyl stretching bands occur at $3800-3000\text{ cm}^{-1}$ and are consistent through exchange, dehydration and rehydration of the samples. Water bending bands occur at $1700-1600\text{ cm}^{-1}$, the details of which have not yet been interpreted in structural terms as they vary in a rather complex fashion from one zeolite to another and from one cation variety to another. The water bands are however expected to fade away during dehydration and reappear during rehydration.

The weak sharp peak at $3750-3740\text{ cm}^{-1}$ which exhibited by all zeolites and has been ascribed (42-44) to a hydroxyl at the external surface or the occluded silica residue, is in evidence in both the X and Y untreated zeolites.

There are also two strong peaks near 3650 and 3550 cm^{-1} . Both are ascribed to framework hydroxyls projecting into the supercage and sodalite-prism complex respectively. Apparently the hydroxyl stretching frequency and hence the bond energy increases as the proton projects into a larger volume. In the X zeolite it was visible at 3680 and in the Y it did not exist. The lower frequency band is visible at $\sim 3575\text{ cm}^{-1}$. The only visible band in the Y zeolite is the high frequency one at $\sim 3680\text{ cm}^{-1}$. This would indicate that the 13X zeolite has fewer hydroxyls projecting into the sodalite cage while vice versa for the Y52 zeolite.

Figure 7a Infrared spectra of Cr Zeolite 13X (---) and Zeolite 13X (—)

Figure 7b Infrared spectra of Cr Zeolite 13X (---) and Zeolite 13X (—)

TABLE 12 Infrared Spectral Characteristics

Sample	Bands (cm ⁻¹)
13X	3800-3000, 3750-3740, 3650, 3575, 3000-2750 (2950, 2850), 2750-2550, 1700-1550, 1675, 1455, 1375, 1300, 1140(sh), 1050-950, 780-700, 775, 725, 660, 630
Y52	3925, 2900, 3800-3000, 3750-3740, 3680, 3650, 3525, 3500-3100, 2500-2200, 2100-1900, 1660-1575, 1525, 1375, 1200-900, 1140, 1050-950, 1020, 780-680, 775, 725, 640
1-Cr ³⁺ (13X) ¹ AD	3800-3000, 3750-3740, 3650, 3570, 3000-2875 (2950, 2850), 2750-2400, 1700-1600, 1450, 1375, 1150(sh), 1050-950, 780-680, 775, 725, 660, 630
1-Cr ³⁺ (13X) ⁴ AD	3800-3000, 3750-3740, 3580, 3000-2750 (2950, 2850), 2750-2500, 1750-1600, 1460, 1375, 1360, 1150(sh), 1050-975, 780-680, 775, 725, 660, 630
1-Cr ³⁺ (Y52) ¹ AD	3800-3000, 3750-3740, 3630, 3575, 3050-2875 (2950(sh), 2925; 2860(sh) 2850), 2850-2500, 1700-1575, 1460, 1350, 1325(sh), 1150(sh), 1050-950, 780-680, 775, 725, 660, 630
1-Fe ³⁺ (13X) ⁴ AD	3800-3000, 3750-3740, 3560, 3050-2775 (2950(sh), 2925; 2840) 2775-2550, 1700-1600, 1450, 1370, 1340(sh), 1150(sh), 1075-975, 760, 720, 660, 630
1-Fe ³⁺ (Y52) ¹ AD	3800-3000, 3750-3740, 3570, 3050-2780, (2940(sh), 2920; 2840), 2750-2550, 1700-1600, 1450, 1360, 1340(sh), 1150, 1080-975, 780-700, 720, 660, 630
(13X)120	3800-3000, 3750-3740, 3570, 3050-2780, (2940(sh), 2920; 2840) 2750-2550, 1700-1600, 1460, 1375, 1360(sh), 1150, 1090-950, 780-700, 780, 720, 660, 630
(13X)120R	3800-3000, 3750-3740, 3570, 3050-2780 (2940(sh), 2920; 2840) 2750-2550, 1675-1600, 1460, 1375, 1360(sh), 1150, 1050-975, 780-700, 720, 660, 630
(13X)(120R) ²	3800-3000, 3750-3740, 3570, 3050-2780 (2940(sh), 2920; 2840) 2750-2550, 1700-1600, 1460, 1375, 1365(sh), 1150, 1050-950, 765-700, 765, 720, 660, 630
(13X)TGA	3800-3000, 3750-3740, 3570, 3025-2790 (2950, 2920, 2850), 2750-2550 (2730, 2650), 1700-1600, 1460, 1470(sh), 1380, 1365(sh), 1150(sh) 1050-975, 760, 760-700, 720, 660, 630

The infrared spectra show that the hydroxyl stretching bands are not affected by the exchange of either chromium or iron on both the 13X and Y52 zeolites. Neither do dehydration nor rehydration of the exchanged zeolites affect this band.

The 3650 cm^{-1} framework hydroxyl (projecting into the supercage) is unchanged upon 24% exchange of chromium onto 13X. However upon 36% exchange the band disappears, as it does upon exchange of iron onto both 13X and Y52. The exchange of chromium onto Y52 shifts the band to 3630 cm^{-1} . The second framework hydroxyl at 3575 cm^{-1} (projecting into the sodalite-prism) in 13X has shifted to 3570 cm^{-1} for both the 24% and 36% exchanged chromium and to 3560 cm^{-1} for the 48% exchanged iron. The shift of the supercage hydroxyl indicates a decrease in the volume of the supercage - most probably due to more cations in Site II. Perhaps one could say that its disappearance in the iron exchanged samples and 36% chromium exchanged 13X means the supercage is filled to capacity but there must be some factor which would explain this shift. The shift of the sodalite-prism hydroxyls indicates a slight corresponding decrease in sodalite prism volume for the 13X and an increase of volume for Y52.

The weak sharp peak at $3750\text{--}3740\text{ cm}^{-1}$ which is exhibited by all zeolites and has been ascribed already to a hydroxyl at the external surface or the occluded silica residue, was in evidence in all samples, regardless of treatment. The fact that it did not disappear could indicate that it is a framework hydroxyl projecting into either the supercage or the sodalite-prism complex, although the higher frequency would suggest the supercage.

In the range $1300-200\text{ cm}^{-1}$ the results show (Table 12) slight shifts to higher frequency upon exchange of chromium and iron into both X and Y zeolites.

The band at 780 cm^{-1} is due to vibration of oxygen bridging bonds connecting the tetrahedra. Because the band is weaker in the exchanged Y zeolite than in the exchanged X zeolite, one may state that the structural framework of the exchanged Y zeolite is weaker than that of the X zeolite. There is no difference in the peak intensity of the unexchanged X and the exchanged X. However the exchanged Y does show a smaller peak than the unexchanged Y. This would indicate that while the X zeolite is unaffected by the exchange, the Y zeolite framework stability is weakened.

However these results must not be accepted at face value as it is known that the heating resulting from the infrared beam during spectral measurement can affect zeolite dehydration.

The infrared results show no change except the predicted sight of the water bending bands in the $1700-1600\text{ cm}^{-1}$ range fading away upon dehydration. The expected regrowth of water bending bands upon rehydration does not occur.

CONCLUSIONS

The structure of NaX is well established by single crystal X-ray diffraction. The sites occupied by Na^+ ions are I and I' with the water in I' and II'. The sites occupied by replacement ions are less well documented because exchange is always carried out on the powdered form and indirect structural methods must be employed. The suggested arrangements however, fall naturally into a progressive pattern of substitution which represent occupation of successively less stable sites. This corresponds directly with the decreasing availability of lattice oxygen ligands in sites I, I', II' and finally II.

This theoretical sequence appears to be confirmed by the current experiments. The infrared spectra show the progressive loss of lattice hydroxyl with increasing exchange levels. At the same time, the free volume of the sodalite cage increases, while that of the supercage decreases and the thermal data show that there is an increase in the lattice water content but a decrease in its stability.

All of these facts are consistent with the occupation first of Site I by the dehydrated exchange ion. This site was formerly occupied by a hydrated $\text{Na}^+(\text{H}_2\text{O})_4$. Those waters of coordination were hydrogen bound to the lattice oxygen of the sodalite cage. This aquated ion has been expelled by the much larger deaquated exchange ion binding directly to the lattice oxygen. Thus the O---H bonds are all broken, the sodalite cage is now empty of water, and the water in the supercage from both the exchange ion and the displaced sodium ions is more weakly bound.

For the exchange ion the next most stable site is I' or II', both providing three lattice oxygen and three waters in the supercage. Site II' is occupied first if Site I is occupied because of Coulomb repulsion. Up to this level of exchange one would expect dilute magnetic behaviour. Immediately Sites I and I' are occupied, because II' is also occupied, exchange ions become adjacent in the lattice, sharing lattice oxygen bridges on alternate sides of the 6-ring. This provides the opportunity for shared oxidation states (mixed valence states in partly reduced species) and the formation of metal-metal bonded dimers. Such dimers do not form between pairs of Cr(III) ions, but do form in mixed valence or pairs of Cr(II) ions (45).

The bridging provided by the lattice can stabilize these dimers and lead to reduction at very low temperatures. Evidence of this is seen in the progressively graying colour of the doped materials and the falling magnetic susceptibility, to be expected in the formation of diamagnetic Cr(II) dimers.

At the highest levels of exchange, Site II must also be occupied. This can displace the ion in Site II' towards that in Site I providing a further opportunity for dimerization. Such metal-metal bond formation could readily distort the supercage, as is observed at the highest exchange achieved in these experiments, by powder crystallography.

There are distinct differences seen in the DTA spectra of the original exchanged zeolites and the rehydrated zeolites for both X and Y. The infrared spectra do not show the expected regrowth of water bending bonds, again indicating a breakdown of the bridging hydroxyls. This is further indication of lattices which have been irreversibly created.

In conclusion, it appears that the reduction suggested by the Union Carbide research proceeds very easily once dimer formation is possible at the higher levels of exchange. It appears to be completely irreversible. This is because the lattice collapses to a new form and is incapable of breaking the Cr(II)-Cr(II) bond when reoxydation is attempted.

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