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EXAFS STUDY OF Ni EXCHANGED INTO ZEOLITE Y

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Abstract

EXAFS and near edge spectroscopy were used to monitor changes in Ni coordination as a function of treatment conditions after aqueous exchange into zeolite Y. Our results suggest that after calcination and dehydration under the conditions of this study, major site occupancy for Ni appears to be in the tri-coordinate exchange sites, and not in the hexagonal prisms as suggested by previous x-ray diffraction results.

Introduction

Cation exchange sites for zeolite Y are well documented (1) and include the hexa-coordinate SI site in the center of the hexagonal prism as well as a number of tri-coordinate sites (SI', SII, SII' and others) primarily associated with single six rings of the sodalite cage. Previous studies using x-ray diffraction (2,3) have demonstrated that site population is dependent on the type of cation exchanged and the conditions of treatment following the exchange. Cation coordination and bond distance were determined by averaging over all exchange sites, both occupied and unoccupied. In this work we examined the local environment of Ni^{+2} exchanged into zeolite Y as a function of various thermal treatments using EXAFS.

Experimental

Ni exchanged zeolite Y (Si/Al=2.65) was prepared by equilibration of NaY with 0.1 N $Ni(NO_3)_2$ at room temperature, to a loading of 6.7 wt%, followed by water washing and drying in air at 25°C (NiYh). This sample was then air calcined at 400°C followed by back-exchange with Ca^{+2}, reducing the Ni level to 2.1 wt% (NiYch). Two other samples were prepared by 550°C vacuum dehydration for 10 hrs. of the initial Ni exchanged material and of the calcined, Ca^{+2} back-exchanged material (NiYd, and NiYcd). The dehydrated samples were kept air and moisture free prior to and during data collection. EXAFS data were obtained at -175°C at the NSLS at a ring energy of 2.4 GeV with electron currents of 40-70 mA. Analysis of the data was performed following published procedures (4).

Results and Discussion

Upon initial exchange of the zeolite, Ni^{+2} is hexa-coordinate with oxygen from water molecules, with an average Ni-O bond distance of 2.04 Å. No outer shell scattering due to other Ni atoms or the zeolite framework is observed indicating a nonuniform orientation of the cation within the zeolite supercage. The Ni K edge spectrum of the initial exchanged material is identical to that of $Ni(H_2O)_6^{+2}$ as are the Fourier transformed EXAFS modulations (Ft), as shown in Figures 1a,b.

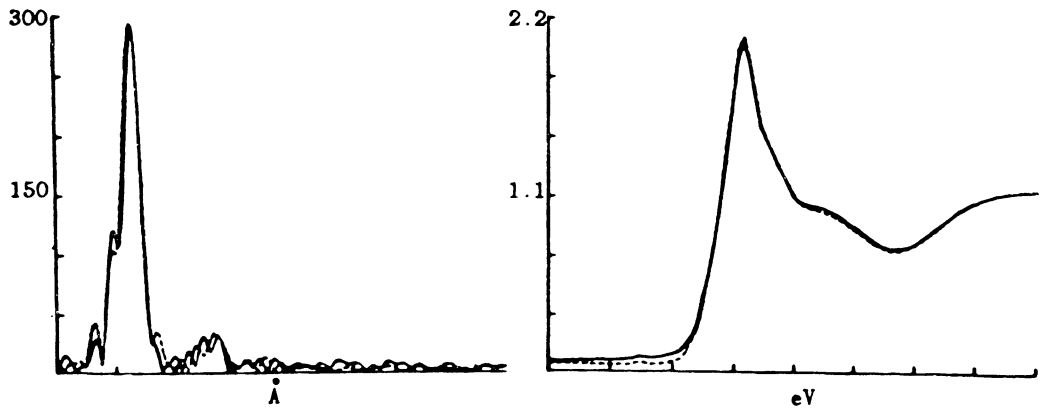

Figure 1. Comparison of Fourier transformed, k^3 weighted EXAFS modulations and K edge spectra for the reference compound $Ni(H_2O)_6(NO_3)_2$ (solid line) and Ni exchanged zeolite after RT drying (NiYh, dashed lines).

Calcination and Ca^{+2} back exchange causes the average Ni-O coordination to decrease to four, at a distance of 2.07 Å, concomitant with the appearance of significant outer shell scattering from Si(Al) and O atoms of the zeolite framework (Fig. 2a). The distances and coordination numbers are consistent with Ni^{+2} ligated to three framework oxygens and one water molecule. The decrease in K edge intensity (Fig. 2b) is consistent with Ni^{+2} binding at a low symmetry (C_{3v}) site. The anchoring of Ni to the framework gives rise to the outer shell scattering in the 3-4 Å region.

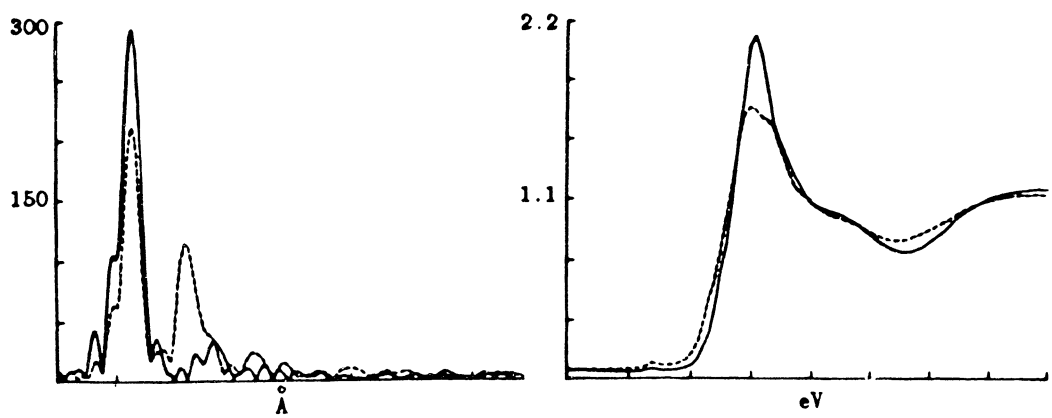

Figure 2. Comparison of Fourier transformed, k^3 weighted EXAFS modulations and K edge spectra for the Ni exchanged zeolite after drying (NiYh, solid lines) vs. sample after calcination and Ca^{+2} back-exchange (NiYch, dashed lines).

Dehydration of this material causes loss of one oxygen atom from the first coordination sphere, presumably due to the removal of ligated water, and a slight contraction of the average Ni-O bond length to 2.02 Å. Little change occurs in the K edge intensity due to dehydration. The Ft and edge spectrum for the calcined, dehydrated material are shown in Figures 3a,b.

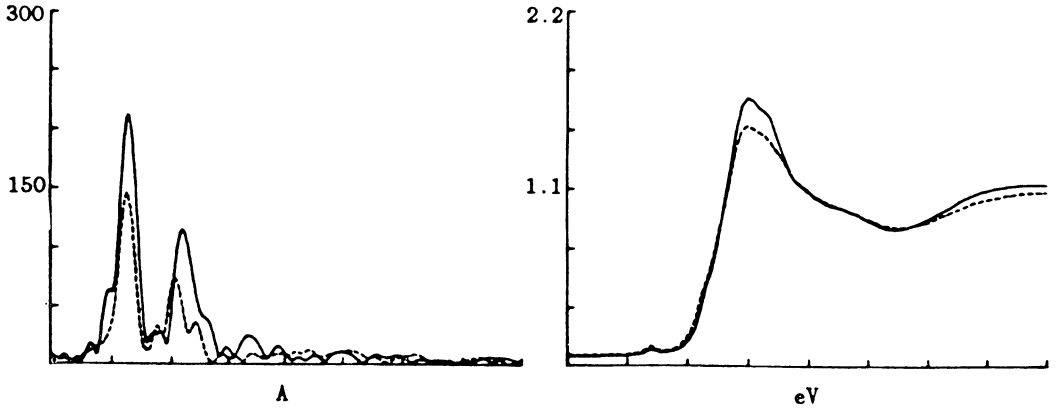

Figure 3. Comparison of Fourier transformed, k^3 weighted EXAFS modulations and K edge spectra for the calcined, Ca^{+2} back-exchanged NiY samples before (solid lines) and after (dashed lines) dehydration.

Direct dehydration of the Ni^{+2} exchanged starting material also gives rise to a Ni species with an average first shell oxygen coordination number of three, though considerably stronger outer shell scattering is observed for this material. In addition, the average Ni-O bond length increases to 2.10 Å, and a considerably more intense edge spectrum is observed, as illustrated in Figures 4a,b. Though the edge spectrum would suggest occupation of a high symmetry site such as SI, significant occupation of this site is inconsistent with the number of coordinated oxygens.

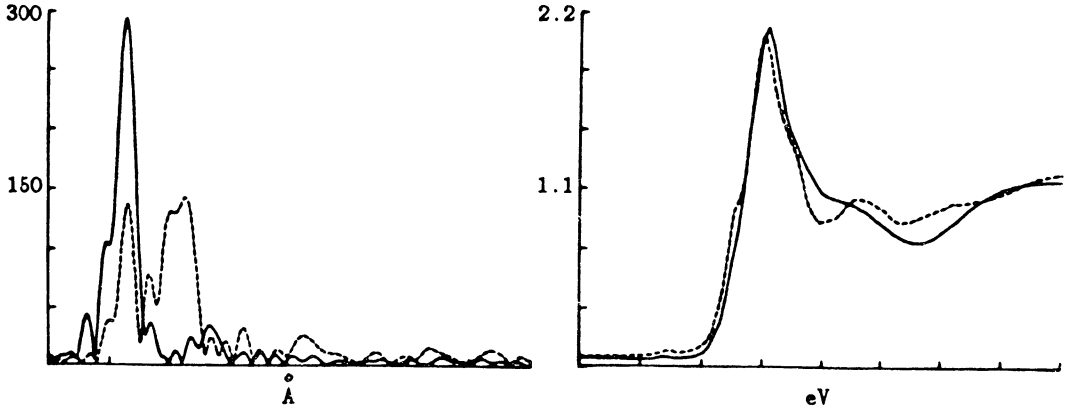

Figure 4. Comparison of Fourier transformed, k^3 weighted EXAFS modulations and K edge spectra for the Ni exchanged starting material before (NiYh, solid lines) and after (NiYd, dashed lines) direct dehydration.

EXAFS results on this series of NiY samples suggests that after initial exchange Ni^{+2} is located in nonuniform positions within the zeolite supercage as a hexa-aquo species. Calcination followed by Ca^{+2} back-exchange leaves only Ni^{+2} atoms that are anchored to the zeolite framework. Dehydration drives off ligated water molecules resulting in Ni^{+2} cations ligated exclusively to framework oxygens. Major cation occupancy appears to be in the three coordinate sites, SI', SII and SII', and not in the hexa-coordinate SI site.

Acknowledgments

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