

Withdrawal of Electron Density by Cations from Framework Aluminum in Y Zeolite Determined by Al XAFS Spectroscopy

D. C. Koningsberger^a and J. T. Miller^b

^aLaboratory of Inorganic Chemistry and Catalysis, Debye Institute, Utrecht University, P.O. Box 80083, 3508 TB Utrecht, The Netherlands

^bAmoco Research Center, 150 W. Warrenville Rd., Naperville, IL 60566-7011, USA

The local Al structure and charge density in Y zeolites have been determined by low energy, Al XAFS spectroscopy. The whiteness intensity indicates that the Al charge density in Y zeolites decreases with increasing charge of the exchanged cation and correlates with the acidity of the zeolite. This result is consistent with the model that polyvalent cations withdraw electron density from the hydroxyl groups increasing their acidity.

1. INTRODUCTION

For most hydrocarbon reactions, alkali metal zeolites, for example Na-Y, are relatively unreactive. Exchange of alkali ions by polyvalent cations like Ca, or La results in increased acidity and catalytic activity. The catalytic activity increases with the increasing charge on the cation [1-3]. Early explanations for the enhancement in activity by cations exchanged into Y proposed that strong electrostatic fields are present within the pores of the zeolite. Because of the rigid structure of the zeolite, the charge on the cation is not fully compensated by the negative charge localized on the aluminum-oxide tetrahedra [4]. Polyvalent cations in low coordination sites were proposed as acid centers [5]. An alternative explanation suggested that cations generate acidic hydroxyl groups by hydrolysis of coordinated H₂O [6,7]. The acidic hydroxyl groups were confirmed by infrared spectroscopy [8].

Exchange of the alkali ions by ammonium ions with subsequent calcination to produce H-Y generates Brønsted acid sites and enhanced catalytic activity compared to Na-Y. In the absence of non-framework Al, however, the catalytic activity of H-Y is low. The activity of H-Y is greatly enhanced by exchange of a small amount of La ions [9,10]. The polyvalent cations, present in the β cages [11], are thought to withdraw electron density from the hydroxyl groups increasing their acidity [9,10,12]. The acid strength and catalytic activity of the Brønsted sites are determined by the polarizing effect of the cation and increases with increasing charge of the cation.

In the present study, the effect of the cation on the charge density of the Al ion and the Al-O bond distance has been determined by Al XAFS spectroscopy. As the charge on the cation increases from Na to H to Ca to La, the electron density on the Al decreases. The

charge on the Al ion parallels the acidity of the catalysts. By contrast, the Al-O bond distance is independent of the type of exchanged cation and was about 1.7 Å.

2. EXPERIMENTAL

Na-Y was a commercial zeolite (LZY-54) purchased from UOP. The sample crystallinity was confirmed by XRD and had a unit cell dimension of 24.676 Å, ca. 56 Al/unit cell. The preparation of H-Y has previously been given [13]. Briefly, Na-Y was repeatedly ammonium exchanged and carefully calcined to give H-Y. The crystallinity by XRD was 98% based on Na-Y as a standard, and the unit cell dimension was 24.643 Å, or 52 Al/unit cell (11.5 wt% Al and 0.13 wt% Na). H-CaY (and similarly H-LaY) were prepared by ion exchange of Na-Y three times by a ten fold excess of 0.5 M Ca(NO₃)₂. The Ca-Y was washed, dried at 100°C overnight and calcined at 300°C for 3h. The Ca-Y was ion exchanged three times with a ten fold excess of 2 M NH₄NO₃, washed, dried and calcined at 300°C for 5 h. The elemental analysis for H-CaY was 11.6 wt% Al, 1.5 wt% Ca, and 0.2 wt% Na, and for H-LaY was 12.4 wt% Al, 12.4% La, and 0.4 wt% Na. Standard methods were used to determine the Si and Al NMR, and the number of acid sites were determined by NH₃ TPD [14].

EXAFS measurements were performed at the soft X-ray XAFS station 3.4 of the SRS at Daresbury (UK). This station is equipped with a quartz, double crystal monochromator, and harmonic contamination of the X-ray beam was minimized by collimating mirrors. The estimated resolution was 1.5 eV at the Al K-edge (1559 eV). The data were collected simultaneously with a fluorescence and an electron yield detector. Data were collected with a k-space scan mode (start, 3 sec.; end, 30 sec.), and six scans were averaged in order to minimize both high and low frequency noise.

Sample preparation, reference compounds, experimental conditions and standard procedures for analysis of XAFS data have previously been reported [13]. The near edge spectra were determined from the electron yield data, and the fluorescence data were used to generate the EXAFS function. The data were analyzed using the latest version of the Utrecht University XAFS Data Analysis Program (XDAP) which allows for fitting in r-space.

3. RESULTS

X-ray diffraction and N₂ micropore volumes indicate that the four Y zeolites are highly crystalline. The Si NMR also indicate that there is little change in the Si/Al ratio of the H-Y, H-CaY and H-La-Y compared with Na-Y. Although the ratio of the peak intensities of H-LaY are unchanged, the resonances are significantly broadened. The Si/Al ratio of all catalysts is about 2.5 [15]. The Al NMR of Na-Y indicate that all of the Al is in tetrahedral coordination. For H-Y, 85% of the Al are in tetrahedral coordination with about 15% in octahedral coordination. The Al NMR of H-CaY indicate that 85% of the Al is in tetrahedral coordination with 10% in octahedral coordination. The remaining 5% Al seems to be in a distorted tetrahedral coordination which appears as a shoulder (about 55 ppm) of the main tetrahedral resonance. For H-LaY, 55% of the Al is in a symmetric tetrahedral coordination,

i.e., a resonance at 60 ppm. Approximately, 10% of the Al is octahedral, 0 ppm, while the remaining 35% of the Al occurs as a broad resonance centered at 30 ppm. Since the Si NMR indicate little loss of structural Al, this 30 ppm peak may be due to structural, tetrahedral Al located near La ions resulting in a distorted electronic coordination about the Al.

For each Al in the lattice, charge balance requires one equivalent of univalent cation. The elemental composition of H-Y, H-CaY and H-LaY indicate that there are 4.2, 4.3 and 4.6 mmol/g of Al, respectively. In addition, the univalent cation charge (due to Na, Ca or La) for H-Y, H-CaY and H-LaY are 0.06, 0.8 and 2.8 mmol/g. The number of protons required for charge balance for each, therefore, is estimated to be 4.1, 3.5 and 1.8 mmol/g. The number of acid sites which strongly chemisorb NH_3 in H-Y, H-CaY and H-LaY were 3.9, 3.6, and 1.9 mmol/g, respectively, and is equivalent to the number of protons in each catalyst. In H-CaY and H-LaY the cations, Ca^{+2} and La^{+3} , do not chemisorb ammonia and are not strongly acidic.

The x-ray absorption near edge spectra (XANES) of Na-Y (solid line), H-Y (dotted line), H-CaY (dashed line), and H-LaY (dot-dash line) are given in Figure 1. There is a clear distinction in the white line of the four samples with the intensity increasing in the order Na-Y < H-Y < H-CaY < H-LaY.

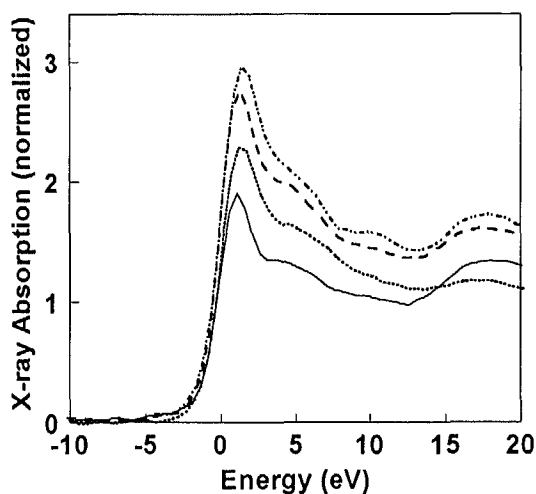


Figure 1. X-ray Absorption K-edge of Al (Normalized) for Na-Y (solid line), H-Y (dotted line), H-CaY (dashed line) and H-LaY (dot-dash line).

Figure 2a and 2b show the average EXAFS spectrum and the Fourier transform of Na-Y (solid line) and H-CaY (dotted line), respectively. The high signal-to-noise ratio of the EXAFS data allows for the detection of higher coordination shells. The node positions for the two catalysts are nearly identical and indicate little difference in the Al-O bond distance which is confirmed in the Fourier transform. The lower amplitude of the first shell Al-O peak in the Fourier transform of H-CaY indicates a larger distortion in the Al-O coordination in

comparison to that in Na-Y. Similarly, Figure 3a and 3b compare the EXAFS spectrum and Fourier transform for H-CaY (solid) and H-LaY (dotted). Again, the node positions of the two catalysts indicate little difference in the Al-O bond distance. The amplitude of the first shell Al-O peak of H-LaY is slightly lower than that of H-CaY indicating a slightly larger distortion of the Al-O coordination.

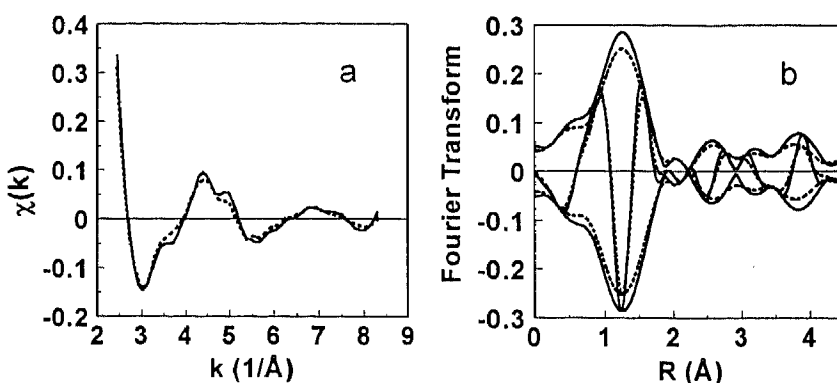


Figure 2. a) Raw EXAFS data, and b) Fourier transform (k^1 : $\Delta k = 2.7-8.2 \text{ \AA}^{-1}$) of Na-Y (solid line) and H-CaY (dotted line).

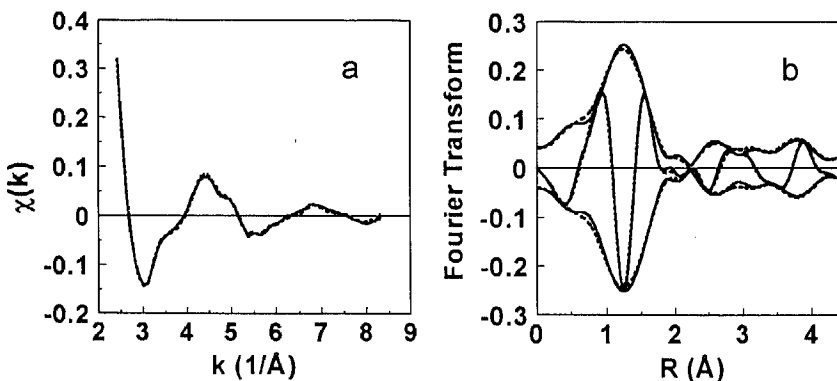


Figure 3. a) Raw EXAFS data, and b) Fourier transform (k^1 : $\Delta k = 2.7-8.2 \text{ \AA}^{-1}$) of H-CaY (solid line) and H-LaY (dotted line).

The first shell Al-O peak in the Fourier transform of the zeolite samples were fit in r -space (both magnitude and imaginary parts) using a non-linear multiple shell fitting routine [13]. All catalysts were fit over the same data range (k^1 weighted, $\Delta R = 0.5 - 2.0 \text{ \AA}$, $\Delta k = 2.7 - 8.3 \text{ \AA}^{-1}$). The number of independent parameters ($N_{\text{indp}} = 2 * \Delta k * \Delta R / \pi + 1$) was 6.3, and the

degrees of freedom ($N_{\text{free}} = N_{\text{indp}} - N_{\text{fit}}$) were 2.3. The first shell fit in r-space is given in Figure 4a for H-LaY. The data and the fit were inverse Fourier filtered over the same r-range and are compared in Figure 4b. The quality of the fits is typical for all catalysts. The coordination parameters are given in the Table. Systematic errors are minimized by using the same background subtraction and normalization procedures for all data sets and by calibration with the reference phase shift and back-scattering amplitudes. Although fitting in r-space increases the useful data range, at present, it is not possible to calculate the limits of accuracy. For all Y zeolites, the Al-O coordination number is 4 in agreement with tetrahedral coordination. In addition, the Al-O bond distance for all catalysts is similar, around 1.7 Å, also consistent with an Al-O tetrahedral coordination. The disorder (Debye-Waller factor) in the Al-O coordination increases in the order Na-Y < H-CaY < H-LaY.

Table
Coordination Parameters

Parameters	N	$\Delta\sigma^2$ ($\times 10^3$) (Å ²)	R (Å)	ΔE_0 (eV)
Coordination: Al-O				
Na-Y	4.0	-0.004	1.70	1.4
H-CaY	3.9	-0.002	1.71	-0.5
H-LaY	4.1	0.000	1.70	-0.3

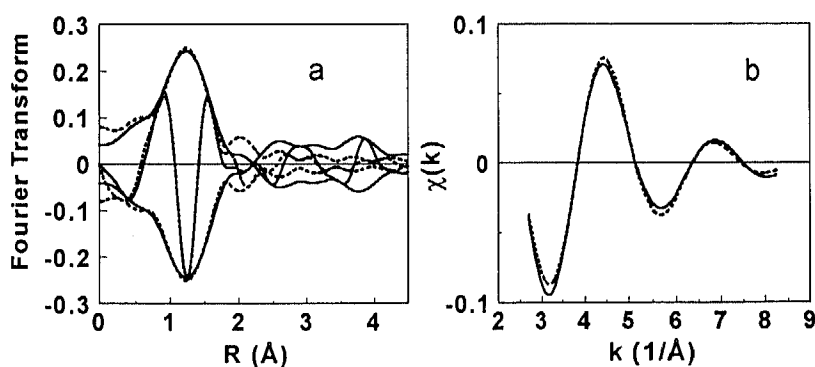


Figure 4. Results of fit in r-space (k^1 : $\Delta k = 2.7\text{-}8.2 \text{ \AA}^{-1}$, $\Delta R = 0.5\text{-}2.0 \text{ \AA}$) for H-LaY (data: solid line, and fit: dotted line). a) Fourier transform, and b) Fourier filtered data from 4a.

4. DISCUSSION

As shown in Figure 1 the white line intensity, representing a 1s to 3p transition, is sensitive to the type of cation exchanged into the zeolite. The white line intensity is the highest for H-LaY and increases in the order Na-Y < H-Y < H-CaY < H-LaY. Previously it was shown for H-Y and Na-Y that the whiteline intensity was higher for H-Y than Na-Y [13]. For these catalysts, the order of the electron densities derived from the white line intensities is in agreement with theoretical calculations for zeolite clusters. For example, the positive charge on the Al in a protonated aluminosilicate ring, $H^+ AlSiO_3(OH)_6^-$, is 1.52 while on a symmetrically coordinated Na-aluminosilicate ring, $Na^+ AlSiO_3(OH)_6^-$, the Al charge is 1.43, or 0.09 electrons less on the protonated cluster [16]. The whiteline intensities in this study, therefore, indicate that the electron density on the Al is lowest, or positive charge of the Al ion is highest, for H-LaY and increases in the order H-LaY < H-CaY < H-Y < Na-Y.

Structural determination of the Al-O bond distance in H-LaY, H-CaY and Na-Y indicate that the average distance is very similar, 1.70, 1.71, and 1.70 Å, respectively. Previously, the Al-O bond distance in Na-Y was reported as 1.62 Å [13]. The longer distance reported here is due to better data quality and the different fitting procedure, i.e., fitting in *r*-space. The current fluorescence data show a more linear response with increasing energy allowing for more accurate background subtraction. In addition, for Al in zeolites, the maximum data range for EXAFS analysis is limited up to about 8.5 Å⁻¹ due to the overlap of the Si K-edge. Fourier filtering for fitting in *k*-space, however, limits the useful data range to about 3.5 Å⁻¹ [13]. By fitting in *r*-space, the useful data range can be increased by about 2 Å⁻¹ improving the accuracy of the Al-O bond distance determination. Applying this new procedure to the previous data obtained on Na-Y results in an Al-O bond distance of 1.68 Å in general agreement with the results from this study. Reanalysis of the previous EXAFS data of H-Y results in an Al-O distance of 1.67 Å. The current results indicate that within the limits of accuracy the Al-O bond distance is not sensitive to the type of cation exchanged into the zeolite.

The whiteline intensity indicates that the cation has a dominating effect on the electron density of the aluminum ions. The order of the electron density parallels the acidity of the catalysts. That is, the electron density of the aluminum ion is the lowest and the whiteline intensity is highest for the most highly acidic zeolite, e.g., H-LaY. Since the cations are coordinated to lattice oxygen ions, it is likely that the cations are withdrawing aluminum electron density through these coordinated oxide and hydroxide ions. The low electron density on the aluminum ion also suggests that the electron density of the lattice oxide ions is lower due to coordination with the cation. Since the acid sites in H-CaY and H-LaY are due to the protons, the correlation of the whiteline intensity with the acidity suggests that a higher acid strength in ion-exchanged Y is due to withdrawal of electron density from the hydroxyl groups by the nearby polyvalent cations consistent with the model for enhanced acidity proposed by Lunsford [9,10,12].

5. CONCLUSION

Low energy Al XAFS spectroscopy is a powerful technique for directly measuring the local Al-O bond distance and charge on the Al ion. The average Al-O bond distance determined by EXAFS spectroscopy is independent of the type of exchanged cation in zeolite Y. On the other hand, the whiteline line intensity is very sensitive to changes in the charge on the Al ions induced by exchanged cations and correlates with the catalyst's acidity. As the charge on the cation increases, the charge on the Al decreases suggesting that polyvalent cations withdraw electron density from the Al through the oxygen ions. The correlation of the whiteline intensity with the acidity suggests that the origin of the enhanced acid strength is due to the withdrawal of electron density from acidic hydroxyl groups by the nearby polycation.

REFERENCES

1. R.C. Hansford and J.W. Ward, *J.Catal.*, **13**, (1966) 316.
2. P.E. Eberly Jr. and C.N. Kimberlin, *Adv. Chem. Ser.*, **102**, (1971) 374.
3. M.L. Poustma, *Zeolite Chemistry and Catalysis*, ACS Mono. **171**, J.A. Rabo (ed.), ACS, Washinton, D.C., (1976) 437.
4. J.A. Rabo, P.E. Pickert, D.N. Stamires, and J.E. Boyle, *Proc. 2nd Int. Cong. Catal.*, Editions Technip, Paris, **II** (1961) 2055.
5. P.E. Pickert, J.A. Rabo, E. Dempsey and V. Schomaker, *Proc. 3rd Int. Cong. Catal.*, W.M.H. Sachtler, G.C.A Schuit and P. Zwietering, eds., North-Holland Publishing Co., Amsterdam, **I** (1965) 714.
6. C.S. Plank, , *Proc. 3rd Int. Cong. Catal.*, W.M.H. Sachtler, G.C.A Schuit and P. Zwietering, eds., North-Holland Publishing Co., Amsterdam, **I** (1965) 727.
7. P.A. Jacobs, J.B. Uytterhoven, *J. Chem. Soc., Faraday*, **69**, (1973) 373.
8. J.W. Ward, *J. Catal.*, **10**, (1968) 34.
9. J.H. Lunsford, *Fluid Catalytic Cracking II, Concepts in Catalyst Design*, ACS Sym. Ser. 452, M.L. Occelli (ed.), ACS, Washington D.C., (1991) 1.
10. R. Carvajal, P.-J. Chu and J.H. Lunsford, *J. Catal.*, **125**, (1990) 123.
11. A.K. Cheetham, M.M. Eddy and J. M. Thomas, *J. Chem. Soc., Chem. Commun.*, (1984) 1337.
12. P.O. Fritz and J.H. Lunsford, *J. Catal.*, **119**, (1989) 85.
13. D.C. Koningsberger and J.T. Miller, *Catal. Lett.*, **29**, (1994) 77.
14. B.L. Meyers, T.H. Fleisch, G.J. Ray, J.T. Miller, and J.B. Hall, *J. Catal.*, **110**, (1988) 82.
15. Engelhardt, G.; Michel, D. *High Resolution Solid-State NMR of Silicates and Zeolites*; John Wiley and Sons, 150 (1987).
16. R.A. van Santen, B.W.M. van Beest and A.J.M. de Man, *Guidelines for Mastering the Properties of Molecular Sieves*, D. Barthomeuf (ed.), Plenum Press, New York, (1990) 201.