

Characterization of Basicity in Alkaline Cation Faujasite Zeolites—An XPS Study Using Pyrrole as a Probe Molecule

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An X-ray photoelectron spectroscopic method is proposed for the characterization of Lewis basic sites in alkali-cation faujasite zeolites. The method consists of deconvoluting the N_{1s} XPS line of chemisorbed pyrrole and measuring the relative intensities of the peak components. It was found that whenever the zeolite sample contains two kinds of alkali cation, two different deconvoluted N_{1s} peaks corresponding to pyrrole chemisorbed on these two sites are obtained. Combined with previous infrared observations, the results offer further evidence for the basic sites being the framework oxygens adjacent to the alkali cations in faujasite zeolites. The stronger the basic site, the lower the N_{1s} binding energy level of the corresponding peak component is. An N_{1s} peak corresponding to polymerized pyrrole species was also detected in the cases of LiY and NaY zeolites. © 1992 Academic Press, Inc.

INTRODUCTION

Several techniques have been applied to measure the basicity of zeolites, such as infrared spectroscopy (1–3), microcalorimetry (4), and photoelectron spectroscopy (5–7). For example, Vinek *et al.* (7) measured the EPD strength (electron pair donor strength, i.e., the Lewis basicity) of MgNaX and MgNaY zeolites by the O_{1s} binding energy. The result indicated a stronger EPD ability of oxygens in zeolites than in SiO₂–Al₂O₃. Similar observations were extended to a series of alkaline cation X zeolites by Barr and Lishka (5) and Okamoto *et al.* (6). The former authors suggested that the shift of O_{1s} as well as Si_{2p}, Al_{2p}, and Na_{1s} binding energy was associated to the complex subunits present in the aluminosilicate system rather than simply due to the individual elements, the aluminate subunits working as anionic groups while silicate units acted as cationic groups. Okamoto *et al.* concluded that the basic strength of framework oxygens increased with Al con-

tent regardless of the crystal structure. However, it is noted that the shift of O_{1s} binding energy reported in these works is not very large. For example, the difference in O_{1s} B.E. between LiNaX and CsNaX samples is only 0.7 eV, the FWHM of O_{1s} peaks in all cases being also relatively narrow (less than 2.5 eV). Thus further extraction of the information about basicity in zeolites could become difficult if only the O_{1s} B.E. is taken under consideration. Different XPS methods in combination with more usual techniques should be required to provide a comprehensive picture of the basic sites in zeolites.

Recently, following the pioneer works of Scokart and Rouxhet (8), and Barathomeuf (1, 2), a detailed infrared study (3) was performed in our laboratory to characterize the basic sites in alkaline cation zeolites, using pyrrole as an acid probe molecule. In this method a strong colinear NH–O bonded complex is formed between chemisorbed pyrrole and the basic framework oxygen, which results in a significant bathochromic shift of infrared NH stretching band and appearance of some characteristic bands in the ring-stretching region of chemisorbed pyr-

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role. The results indicated that the shift of NH frequency strongly depends on the counter cation in the zeolite. Moreover, the coexistence of two kinds of alkali-cations produces two different NH bands in the same zeolite sample. This fact suggests that the basic properties in zeolites are mainly determined by the local environment rather than the zeolite lattice. In other words, the framework oxygens adjacent to alkaline cations are the Lewis basic sites in zeolites, as their basic strength changes from site to site when different cations are simultaneously present in the same zeolite sample. The basic strength of oxygen sites adjacent to cations increased in the order $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$. Apparently, pyrrole chemisorption must be accompanied by a charge transfer between basic sites (electron donor) and the pyrrole molecule (electron acceptor). A more direct observation of the charge transfer would be expected from the shift of the N_{1s} level of pyrrole molecule in XP spectroscopy. Therefore we report here an XPS study of pyrrole chemisorbed on the alkaline cation faujasite zeolites.

EXPERIMENTAL

Zeolite Samples and Pyrrole Chemisorption

Various alkaline-cation-exchanged X and Y zeolites were prepared from the sodium forms contacted with the corresponding chloride solutions. The exchange temperature was maintained at 70–80°C and the time for a single exchange was around 24 hr. In some cases up to three successive exchanges were performed in order to obtain high exchange levels. The chemical compositions of all samples were determined by atomic absorption spectrophotometry.

Before XPS experiments zeolite samples were pressed into self-supported wafers of roughly 10 mg. These wafers were mounted in a pyrex vacuum cell which was then connected to a vacuum line. The samples were degassed at 400°C overnight and then cooled in vacuum (10^{-5} Torr) to 65°C. The pyrrole vapour was introduced at this temperature

for 2 hr. The cell containing pyrrole vapour was then disconnected from the vacuum line and put in a glovebox. The wafer was transferred into an XPS cell under flowing argon.

XPS Measurements

Gold deposited onto fresh zeolite samples was used as a calibrant for determining the absolute binding energies in XPS experiments ($\text{Au}_{4f_{7/2}} = 84.0$ eV). The deposition was performed under vacuum (10^{-3} Torr) and the thickness of the gold layers was around 20 Å. The XP spectra of pyrrole chemisorbed samples were usually recorded at liquid-nitrogen temperature (-196°C) in order to avoid the easy desorption of chemisorbed pyrrole under the high vacuum of the spectrometer chamber (less than 10^{-8} Torr). For these samples the C_{1s} level was taken as the reference binding energy. A V.G. Scientific Escalab Mark II system with a hemispherical analyzer operated in the constant pass energy mode (20 eV) was employed. An $\text{MgK}\alpha$ X-ray source ($h\nu = 1253.6$ eV) was operated at 20 mA and 15 kV.

The intensity of various XPS bands was determined using linear background subtraction and integration of peak areas. N_{1s} peaks were deconvoluted into two or three components by keeping the same value for the full width at half maximum (FWHM) of all component peaks in a particular spectrum and assuming that the component peaks had Gaussian–Lorentzian shape. In this deconvolution operation the FWHM value adopted for all the component peaks of the N_{1s} lines was 2.4 eV because all Si_{2p} , Al_{2p} , and Na_{1s} lines recorded showed an FWHM value less than or equal to 2.4 eV. Deconvolution was performed using the VGS-1000 software.

Gravimetric Adsorption Measurements

Gravimetric pyrrole adsorption capacity measurements were carried out using a microbalance MTB 8 (Setaram, France) connected to a conventional vacuum system. About 100 mg of the sample was placed in a Pyrex bucket and degassed at 400°C over-

night. Then the sample was cooled down to room temperature and pyrrole vapour was admitted to the system for about 20 min. Finally, physisorbed pyrrole was desorbed by pumping at 65°C until no change in weight was observed.

RESULTS AND DISCUSSION

XPS binding energy determination for nonconductive materials requires a correction for a shift in the energy scale due to charging. It appears that no universally accepted technique of correction for the charging effect in insulators is available yet. Employing an electron flood gun to remove the charging shift was recommended by Barr and Lishka (5), but a recent report (9) revealed a chemical instability of the zeolite system upon using this technique. For example, the sodium cations of an NaY sample migrated to the surface region and were further reduced to metal state by the higher energy (above 6 eV) electron bombardment. Another convenient method is the utilization of an internal reference binding energy, such as Si_{2p} for a high-silica zeolite or the C_{1s} level of adventitious carbon. However, the Si_{2p} level varies with the Al content for low-silica zeolites (5, 6), and the uncertainty of the C_{1s} level which depends on the sample history was also criticized. The technique of doping the surface of zeolites with a pure conductive element of known binding energy, e.g., Au, is often used for the correction (10), this method was also employed in this work. Carefulness must however be exercised because a thick doping will cover the sample and erase the XPS signals (11), while a thin doping could result in the formation of isolated gold particles which often do not have their Fermi edge coupled to that of the spectrometer (5). Uwamino and co-workers (11) recommended that the optimum thickness of gold deposited onto a nonconductive sample surface is ~9 Å (path length). It was also noticed that the apparent binding energy of gold deposited on NaF sample remained nearly same when the thickness ranged from 9 to 24 Å (11), there-

fore the thickness of gold deposited on fresh zeolite samples in this work was chosen as ~20 Å. Since the main carbon signals observed on chemisorbed zeolites did not come from the adventitious contamination but from the pyrrole species chemisorbed on basic sites (see below), the C_{1s} level was taken as reference level to calculate the binding energies for zeolite samples after pyrrole chemisorption. Following Barr and Lishka's (5) argument this level was taken as 284.4 eV. For the same zeolite the Si_{2p} and Al_{2s} binding energies of fresh and pyrrole chemisorbed samples are the same in the error range (±0.2 eV), while the difference in O_{1s} binding energies is slightly larger but still less than 0.4 eV.

Table 1 summarizes the XPS results of different alkaline faujasite zeolites. The surface atomic ratios of Si/Al, N/Al, and C/N were estimated using the relation

$$\frac{M_1}{M_2} = \frac{A_1 \sigma_2 \lambda_2 \left(\frac{E_{K1}}{E_{K2}} \right)^{1/2}}{A_2 \sigma_1 \lambda_1}, \quad (1)$$

where M_1 and M_2 stand for different elements, and A , σ , λ , and E_K are the normalized XPS peak area, the cross section of the photoelectron emission, the photoelectron mean free path, and the photoelectron kinetic energy, respectively. The surface Si/Al ratio is slightly larger than the bulk one for almost all samples. In particular, the LiX and LiY zeolites possess the largest surface Si/Al ratio. Taking into consideration the accuracies of the theoretical parameters σ and λ , and XPS intensity ratio, it is concluded from Table 1 that with the alkaline cation faujasite zeolites the surface Al concentration is very close to that of the bulk, but perhaps slightly depleted, particularly for Li exchanged samples. The bulk N/Al ratios were determined from the gravimetric measurements after adsorption and following evacuation at 65°C. Previous infrared results (3) showed that the physisorbed pyrrole would be desorbed after evacuation at this temperature. The number of framework Al atoms is equal to that of

TABLE 1
XPS Results

Sample	Unit cell cation composition	Binding energy (eV)/FWHM (eV)					Atomic ratio				
		Si _{2p}	Al _{2p}	Na _{1s}	O _{1s}	N _{1s}	Si/Al		N/Al		C/N
							Bulk	Surface	Bulk	Surface	Surface
X zeolites											
LiX(P)	Li _{54.3} Na _{31.1}	102.5/2.2	74.5/2.1	1072.3/2.4	531.6/2.3	400.0/3.0	1.25	1.95	0.30	0.11	6.4
(F)		102.6/2.2	74.7/2.2	^b	532.0/2.5			1.61			
NaX(P)	Na _{85.4}	102.2/2.3	74.0/2.1	1072.3/2.3	531.2/2.3	399.9/2.7	1.25	1.43	0.40	0.08	8.0
(F)		102.2/2.2	73.8/2.1	1072.5/2.4	531.6/2.3			1.32			
KX(P)	K _{48.3} Na _{37.1}	101.8/2.2	73.7/2.1	1071.7/2.3	530.9/2.3	399.5/3.2	1.25	1.48	0.35	0.12	5.7
(F)		101.8/2.1	74.0/2.0	^b	531.2/2.5			1.63			
RbX(P)	Rb _{37.7} Na _{47.7}	101.7/2.4	73.6/2.1	1071.6/2.3	530.9/2.5	399.3/3.3	1.25	1.40	0.36	0.11	6.9
(F)		101.8/2.5	73.9/2.2	^b	531.3/2.6			1.94			
CsX-2(P)	Cs _{28.8} Na _{36.6}	101.6/2.4	73.7 ^a	1071.8/2.4	530.9/2.5	398.9/3.3	1.25	1.54	0.36	0.13	6.6
(F)		101.6/2.4	73.9 ^a	^b	531.3/2.6			1.56			
CsX-3(P)	Cs _{59.9} Na _{23.5}	101.5/2.4	73.7 ^a	1071.4/2.3	530.9/2.6	399.0/3.0	1.25	1.52	0.41	0.25	5.3
Y zeolites											
LiY(P)	Li _{27.8} Na _{26.7}	102.8/2.3	75.0/2.1	1073.0/2.3	532.3/2.5	400.1/2.9	2.52	4.10	0.64	0.46	4.0
(F)		102.8/2.5	^b	^b	532.3/2.8						
NaY(P)	Na _{54.5}	102.7/2.3	74.4/2.1	1072.8/2.4	532.1/2.5	400.2/3.1	2.52	3.00	0.67	0.36	4.3
(F)		102.8/2.3	74.7/2.1	1073.0/2.6	532.4/2.6			2.42			
KY(P)	K _{40.0} Na _{14.5}	102.6/2.3	74.3/2.1	1072.4/2.4	531.9/2.6	400.2/3.9	2.52	2.75	0.66	0.13	5.2
(F)		102.8/2.2	74.3/2.2	^b	532.2/2.7			3.22			
RbY(P)	Rb _{34.3} Na _{20.2}	102.5/2.3	74.3/2.1	1072.3/2.4	531.7/2.6	400.0/3.0	2.52	2.40	0.66	0.17	9.0
(F)		102.5/2.4	74.4/2.2	^b	531.9/2.7			2.50			
CsY(P)	Cs _{37.0} Na _{17.5}	102.3/2.3	73.9 ^a	1072.4/2.3	531.4/2.7	399.6/3.7	2.52	2.74	0.63	0.22	5.4
(F)		102.2/2.3	73.7 ^a	^b	531.4/2.6			2.40			

Note. (P) Pyrrole chemisorbed sample, referenced to C_{1s} = 284.4 eV; (F) Fresh sample, referenced to Au_{4f7/2} = 84.0 eV.

^a The Al_{2p} binding energy was estimated from the Al_{2s} level, because of an overlapping of Al_{2p} and Cs_{4d} bands (Al_{2s} - Al_{2p} = 44.9 eV).

^b Have not measured.

counter alkaline metal cations. Accepting that the basic sites are the framework oxygens adjacent to alkaline cations, further assuming that all Al atoms are in zeolite framework positions and each basic site adsorbs one pyrrole molecule, then the bulk N/Al ratios should be at least equal to one. The observed bulk N/Al ratios significantly lower than one is interpreted as a clear indication that zeolite pore geometry factors play an important role during the pyrrole adsorption. The smallest diameter of pyrrole estimated from structural data (12) is about 4 Å, therefore the molecule cannot enter the sodalite units of faujasite type zeolites, which have an opening of only 2.2 Å (13). The only place where the pyrrole molecule can reside is the supercage which has a window opening of 7.5 Å and an internal diameter of ca. 13 Å (13). There are eight supercages per unit cell, then the bulk N/Al

ratios around 0.36 in X zeolites and 0.65 in Y zeolites indicate about 4 pyrrole molecules in every supercage. Lunsford and co-workers (14) reported that dehydroxylated NaY zeolite adsorbs 24 TMP (trimethylphosphine) molecules per unit cell, which corresponds to three TMP molecules located in every supercage. Previous observation in this laboratory (15) about pyridine (kinetic diameter is about 5 Å) adsorption also revealed that nearly three pyridine molecules entered every supercage of Y zeolites. All these results are consistent with what is observed in this work. However, it is noted that the surface N/Al ratios measured by XPS are lower than the bulk ones, even though all precautions were taken in order to avoid desorption during the sample transfer to the XPS analytical chamber, and the measurements were performed at liquid-nitrogen temperature. In fact, the initial at-

tempt to run the XP experiment at room temperature yielded very poor resolution with a smaller surface N/Al ratio of about 0.04. Compared with pyridine, the adsorption of pyrrole on zeolite surface is relatively weak. For example, 65°C is enough to remove the physisorbed pyrrole species on zeolites and all the chemisorbed pyrrole species (except the polymerized pyrrole species, see below) can be removed at 250°C under a vacuum of 10^{-5} Torr. Thus the lower surface N/Al ratios observed in XP experiments must mean an easy desorption of pyrrole molecules under the high vacuum (10^{-8} Torr) in XPS spectrometer chamber. However, this surface ratio still varied for different samples even though the same operating conditions were employed during the experiments. For X zeolites, the surface N/Al ratio basically increased when the cation was changed from Li to Cs, particularly for CsX-3 sample which has a larger Cs content. The same trend is also true after comparing this ratio of KY, RbY, and CsY samples. Then the conclusion is that the adsorption strength of pyrrole on these zeolite samples increased with the electropositivity (or with the decrease of the electronegativity) of the counter cation. The exception is NaY and LiY samples, they showed a large surface N/Al ratios which will be commented on later. Table 1 also lists the surface ratio in atomic concentration of carbon to nitrogen of the samples after pyrrole adsorption. This ratio was slightly higher for NaX and RbY samples, and ranged from 4.0 to 6.9 for the other samples. The higher values found in particular with NaX and RbY must be associated with the lack of accuracy in the determination of the N_{1s} peak areas, rather than with the presence of incidental carbon. These peaks are indeed weak and obtained at signal to noise ratios of 10 to 15. For comparison, the C_{1s} level was also recorded for the fresh samples, this signal was very weak and the C/Al surface ratio was only about 0.03, while this C/Al ratio is usually around 0.6 and 1.5 for pyrrole chemisorbed X and Y

zeolites, respectively. The surface C/N ratio observed here suggests that most of C and N on the surface come from chemisorbed pyrrole species containing both carbon and nitrogen atoms with a theoretical C/N ratio of 4.

The change in binding energy is also clear from Table 1. In both X and Y zeolites, when the counter cation varied from Li^+ to Cs^+ , the binding energy of all the constituting elements shifted to lower value. These results are consistent with observations of other workers. For example, Okamoto *et al.* (6) reported that the shift in binding energy of Si_{2p} and O_{1s} was relatively large when the Al content of zeolites was increased. Here, the shifts in binding energy of different elements depending on counter cations seem to have similar order. However, difference in FWHM was noticed. When the counter cation varied from Li^+ to Cs^+ , the FWHM basically remained unchanged for Si_{2p} , $Al_{2p(2s)}$, and Na_{1s} , while this value increased from 2.3 to 2.6 eV for the O_{1s} level of X zeolites.

The most remarkable feature in Table 1 is the change in N_{1s} levels with the different alkaline cations. Except LiY and NaY, the maximum binding energy decreased in the order $Li > Na > K > Rb > Cs$, and the peaks were found to be substantially broader (40–70%) and less symmetric than their corresponding Si_{2p} and $Al_{2p(2s)}$ levels. Figure 1 shows the fitted spectra of X zeolites; in all cases, the N_{1s} envelopes could be deconvoluted into two or three components. It is noted that a common component with binding energy at 399.8 eV was present in the spectra of all these samples, particularly, this component peak contributed about 90% to the spectrum area of NaX sample. Another weak but also common component was also found at 401.5 eV for most of the samples. This peak usually contributed about 10% to the total N_{1s} envelope area. There is another main N_{1s} component (except for the NaX sample) beside these common peaks in all the spectra, which changed significantly in binding energy with the

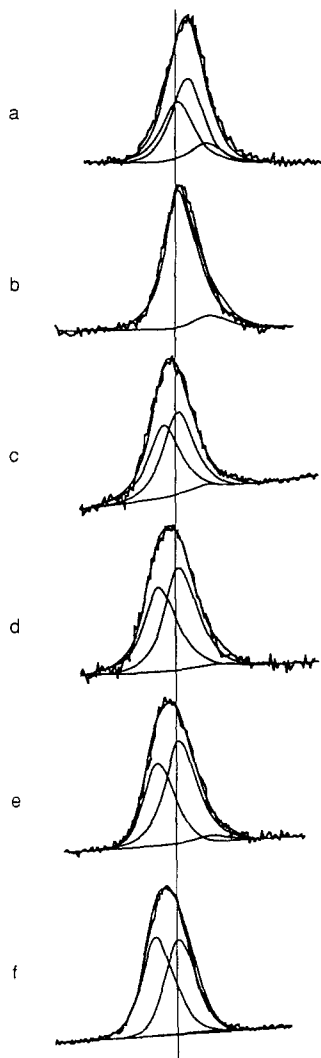


FIG. 1. Deconvoluted N_{1s} XPS spectra of pyrrole chemisorbed on (a) LiX, (b) NaX, (c) KX, (d) RbX, (e) CsX-2, and (f) CsX-3 samples.

counter cations, that is, the binding energy of this component decreased in the order $Li > Na$ (taking the common component which contributed 90% to the spectrum area of NaX) $> K > Rb > Cs$ and the difference of this binding energy between LiX and CsX reached up to 2 eV. Our previous infrared study (3) also showed that a common NH band exists in all the infrared spectra of these samples which all contain residual Na

cations. This band was thus attributed to the pyrrole species chemisorbed on the same kind of basic sites associated with Na cations. The NH band of another pyrrole species chemisorbed on basic sites adjacent to other alkaline cations was also detected. Furthermore, the NH vibration frequencies of these bands were closely related to the corresponding alkaline cations, that is, decreased in the same order: $Li > Na > K > Rb > Cs$. The excellent consistency between the observation by two different techniques strongly offered additional evidence for the assignment of the infrared bands. Vice versa, here the common peak in XPS at 399.8 eV was also attributed to the chemisorbed pyrrole on framework oxygens (basic sites) adjacent to Na cations, while the other main component characterized the basic sites adjacent to other alkaline cations.

Another weak but common component peak indicates the presence of another common adsorbed pyrrole species in all X zeolites. The relatively high binding energy (401.5 eV) suggests that it would be a weakly adsorbed pyrrole species. However, this is not likely to be a physisorbed species, because the lower surface N/Al ratio revealed the desorption of more than 60% of adsorbed pyrrole species under the high vacuum in the spectrometer chamber, among them, the most weakly physisorbed species would be the first to be removed. The infrared spectra (3) also showed the existence of a common NH band with a relatively high wavenumber (3370 cm^{-1}) for all the alkaline cation X zeolites. This band was tentatively assigned to a pyrrole species adsorbed on weaker basic sites, such as the framework oxygen not directly adjacent to a cation. The same assignment could be taken here. However, further work is still required to assign this species.

The situation of Y zeolites is similar (Fig. 2). A common component peak can be found with binding energy around 400.6 eV in the spectra of all Y zeolite samples. Likewise, there is another N_{1s} component beside the common peak in the spectra (this compo-

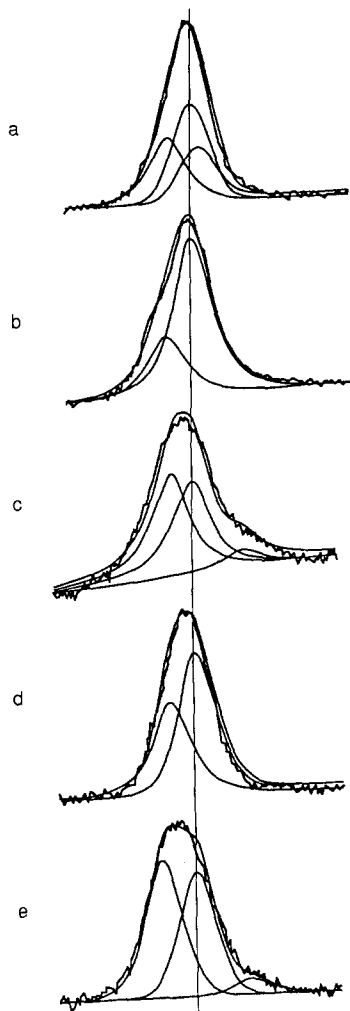


FIG. 2. Deconvoluted N_{1s} XPS spectra of pyrrole chemisorbed on (a) LiY, (b) NaY, (c) KY, (d) RbY, and (e) CsY samples.

ment is the same as the common peak in the spectrum of NaY), which changed its binding energy with the counter cations in the order $Li > Na > K > Rb > Cs$. The infrared results on alkaline Y zeolites also showed a common NH band and another main NH band, which are assigned to the pyrrole species on basic sites associated with different alkaline cations. Similarly, here the common peak in XPS at 400.6 eV was attributed to chemisorbed pyrrole on

framework oxygens adjacent to Na cations, while the other component characterized the basic sites adjacent to other alkaline cations. However, important differences in spectrum deconvolution were noted in the case of NaY and LiY samples. Except for the peaks discussed above, there is another main component peak with a lower binding energy at 399.1 eV. The contribution of this component to the N_{1s} envelope area is about 30%, which is certainly a significant contribution to the large surface N/Al ratio recorded for these two samples. The charge on oxygen in zeolite lattice of these two samples is less than that of the other samples (3), thus the low binding energy cannot be due to the existence of a stronger basic oxygen site. Combined with the fact that these samples possess high surface N/Al ratio, the responsible pyrrole species for this peak should be different in nature. The previous infrared study (3) showed that among the faujasite zeolites a slight polymerization of pyrrole occurred only over these two samples, LiY and NaY. This polymerization is due to the presence of small amounts of acid sites, which is indicated by the weak infrared band at 1490 cm^{-1} after pyrrole chemisorption, while there is no distinguishable NH band corresponding to the acid sites. Polymerized pyrrole is characterized by IR bands at 1445 and 1600 cm^{-1} in the ring-stretching region, and a shoulder band at 3260 cm^{-1} in the NH-stretching region. The results further revealed that a higher temperature favours the polymerization and the polymerized pyrrole species is more stable, and cannot be removed even after desorption at 250°C . In XPS experiments the adsorption of pyrrole was performed at relatively high temperature (65°C) and lasted for 2 hr, which must result in a larger amount of polymerization product than that observed in infrared experiments. Moreover, the high vacuum employed in XPS experiments must also increase the relative concentration of polymerized pyrrole species on the surface of these two samples. The pyrrole polymerization occurs through the connecting between pyrrole rings (16):

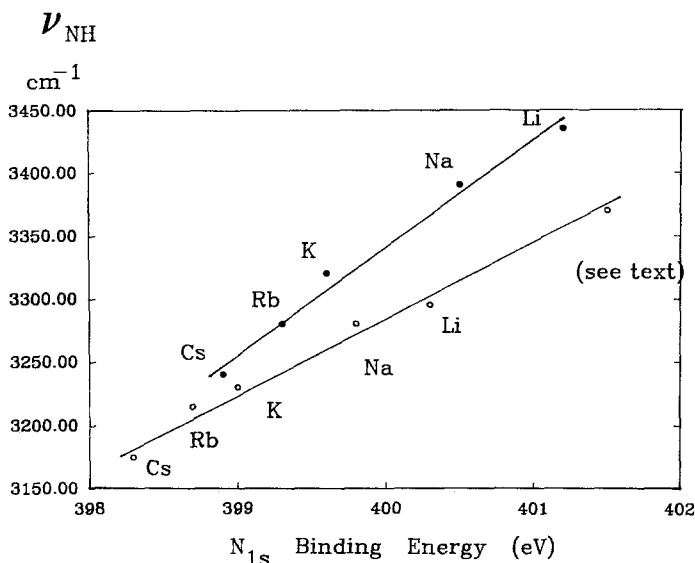
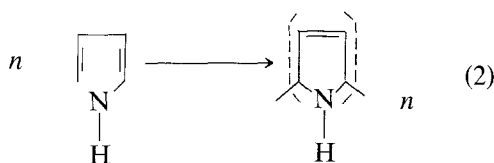


FIG. 3. Relationship between N_{1s} binding energies and NH stretching vibration frequencies of chemisorbed pyrrole on (○) X zeolites and (●) Y zeolites.



Thus the ring structure of the polymerization product possesses less aromatic and therefore more aliphatic character. Pignataro and co-workers (17) reported that the N_{1s} level in pyrrole is higher than that in the corresponding aliphatic compounds. The reason is explained by the less drift of charge from N toward carbon atoms through the π orbital in the aliphatic compounds. The same illustration can be accepted here and then a lower N_{1s} binding energy should be expected for the species corresponding to the pyrrole polymerization product. Table 2 summarizes the deconvolution results and the relative contribution of each component to the total peak area.

The coexistence of two N_{1s} peaks in XPS spectra is in good agreement with the two NH bands observed in infrared spectra for a single zeolite containing two kinds of alkali

cations. This offers further evidence that the framework oxygen adjacent to alkaline cation is the basic site in zeolites. A strong colinear NH-O bonded complex should therefore be formed (12) between chemisorbed pyrrole and this kind of oxygen. The formation of such a complex must be accompanied by the electron transfer from the oxygen to the nitrogen of the pyrrole molecule, which will shift the N_{1s} level to lower energies and weaken the N-H bonding. The evi-

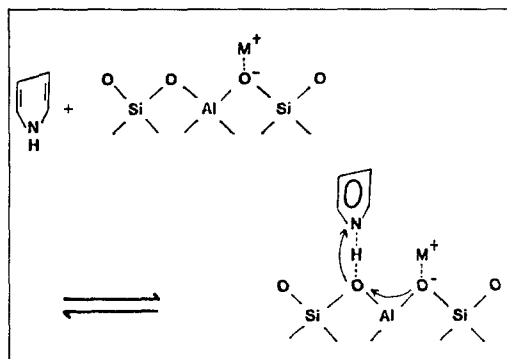


FIG. 4. Model for pyrrole chemisorbed on a basic site.

TABLE 2
Deconvolution of XPS N_{1s} Peaks of Chemisorbed Pyrrole (Binding Energy in eV)

Sample	LiX	NaX	KX	RbX	CsX-2	CsX-3	Assignment
Component 1	399.7	399.8	399.8	399.8	399.7	399.8	Species on basic sites adjacent to sodium cations
Relative intensity%	37.3	87.0	44.0	46.3	51.3	45.0	
Component 2	400.3	399.8	399.1	398.7	398.3	398.3	Species on basic sites adjacent to other alkaline cations
Relative intensity%	50.4	87.0 ^a	43.7	37.1	41.0	51.6	
Component 3	401.5	401.5	401.5	401.6	401.5	401.6	See text
Relative intensity%	12.3	13.0	12.3	16.6	7.7	3.4	
Sample	LiY	NaY	KY	RbY	CsY		Assignment
Component 1	400.5	400.5	400.7	400.5	400.6		Species on basic sites adjacent to sodium cations
Relative intensity%	43.8	70.9	40.2	59.8	43.5		
Component 2	401.2	400.5	399.6	399.3	398.9		Species on basic sites adjacent to other alkaline cations
Relative intensity%	26.2	70.9 ^a	42.3	40.2	47.7		
Component 3	399.1	399.0	<i>b</i>		<i>b</i>		Polymerization product
Relative intensity%	30.0	29.1					

^a The same as component 1.

^b Weak component was found at 403.4 eV for KY and 403.5 eV for CsY, respectively. The former is due to the contribution from K_{2s} (17.5%), the source of the weak peak (8.8%) in the case of CsY remains unresolved.

dence of the weakening of NH bond has been already offered by the bathochromic shift in NH vibration frequency. Here, the shift of N_{1s} binding energy to lower value is also very clear. Figure 3 shows that the shift in binding energy of N_{1s} is well correlated with the shift of NH wavenumber observed in infrared spectra. The basic strength of Lewis base is actually the measurement of its electron donor ability, thus the stronger the basicity of the basic sites, the lower the N_{1s} binding energy. As mentioned before, the N_{1s} level of pyrrole species adjacent to alkaline cations increased in the order $Li < Na < K < Rb < Cs$, which means an increase in basicity of the corresponding basic sites in the same order. A model for chemisorbed pyrrole on basic sites is then suggested as in Fig. 4. Here, the arrow indicates the partial electron transfer direction upon chemisorption.

Question may arise as to the corresponding change in O_{1s} binding energy upon pyrrole chemisorption. Since the increase in electron density on the N atom must mean the reduction of electron density on corresponding framework oxygens, it should cause a shift of the O_{1s} level to higher energies. Compared with the results of fresh samples, the Si_{2p} and Al_{2p} binding energies are the same in the error range (0.2 eV), while the O_{1s} binding energy of samples after pyrrole adsorption is slightly decreased (0.1–0.4 eV). Moreover, the framework oxygens adjacent to different alkaline cations should cause different chemical shifts in O_{1s} binding energy and therefore, as in the case of N_{1s} , the coexistence of two kinds of cations in the same zeolite should result in the broadening of the FWHM. However, both literature data and our results revealed that the change in O_{1s} binding energy and the

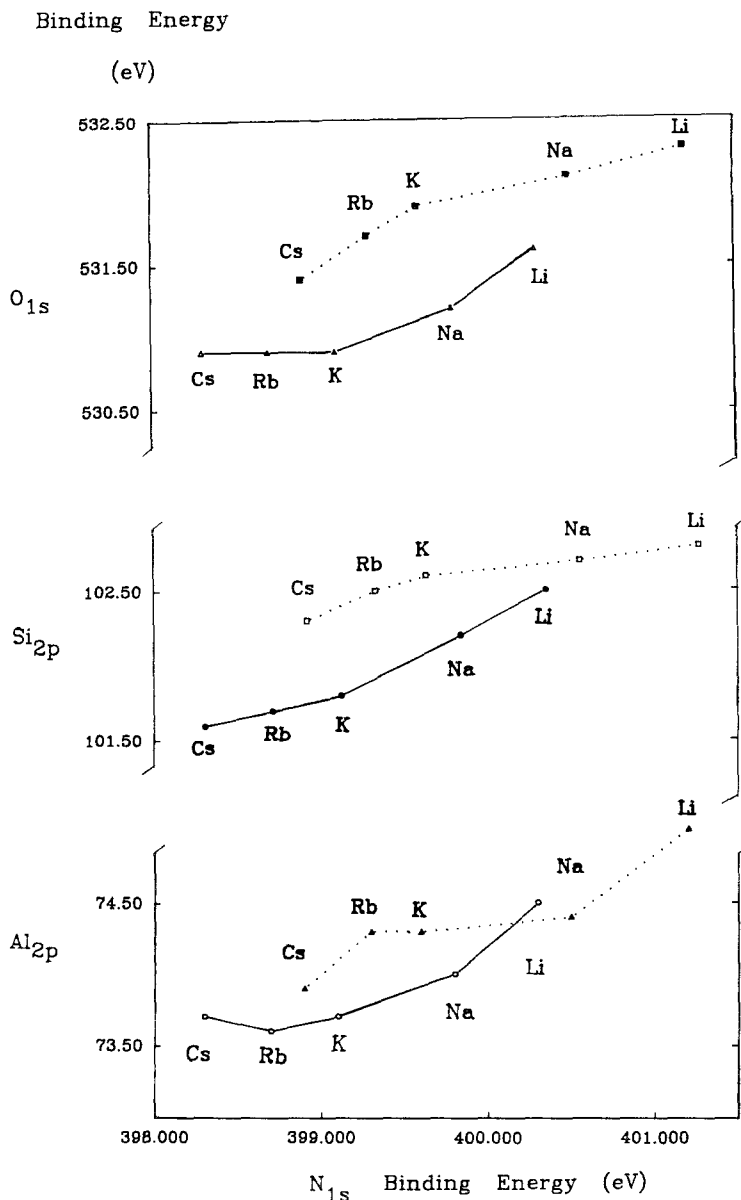


FIG. 5. Changes in binding energies (N_{1s} of chemisorbed pyrrole, O_{1s} , Si_{2p} , and Al_{2p} of zeolites) depending on various alkali cations. Solid line, X zeolites; dashed line, Y zeolites.

FWHM are not very large. The chemical shift of core levels in XPS is approximately described as (18)

$$\Delta BE = k\Delta q - \Delta V, \quad (3)$$

where Δq denotes a change in the electron density, ΔV shows the change in Madelung

potential and here mainly depends on the crystal structure and the Si/Al ratio of zeolites, and k is a constant depending on the element and proportional to e^2/r (r , radius of valence shell). Taking ΔV as a constant for all the zeolite samples in this work, with a fixed Δq the change in binding energy is

mainly determined by the radius of the valence shell. The framework oxygen may be regarded as an O^{2-} anion, then the large radius (1.4 Å) of the anion must result in a small change in binding energy depending on the charge transfer. Vice versa, the relatively large change in N_{1s} binding energy indicates a relatively small radius of N. Our previous work using pyridine to detect acidity in zeolites (15, 19) also suggests that the N_{1s} level is sensitive to the charge transfer, thus the probe molecules containing N atoms seem to be useful indicators of charge transfer in XPS experiments. Figure 5 shows the changes in binding energies of O_{1s} , Si_{2p} , and Al_{2p} levels depending on various alkali cations. Apparently, the largest shift in binding energy is observed in the case of the N_{1s} level, while this shift is relatively small for the other levels.

REFERENCES

1. Barthomeuf, D., *J. Phys. Chem.* **88**, 42 (1984).
2. Barthomeuf, D., and de Mallmann, A., in "Innovation in Zeolite Materials Science" (J. Grobet *et al.*, Eds.), p. 364. Elsevier, Amsterdam, 1988.
3. Huang, M., and Kaliaguine, S., *J. Chem. Soc. Faraday Trans.* **88**, 751 (1992).
4. Rossi, P. F., Busca, G., Lorenzelli, V., Lion, M., and Lavalley, J. C., *J. Catal.* **109**, 378 (1988).
5. Barr, T. L., and Lishka, M. A., *J. Am. Chem. Soc.* **108**, 3178 (1986).
6. Okamoto, Y., Maezawa, M., and Imanaka, T., *J. Catal.* **112**, 427 (1988).
7. Vinek, H., Noller, H., Ebel, M., and Schwarz, K., *J. Chem. Soc. Faraday Trans 1*, **73**, 734 (1977).
8. Scokart, P. O., and Rouxhet, P. G., *J. Chem. Soc. Faraday Trans 1*, **76**, 1476 (1980).
9. Edgell, M. J., Paynter, R. W., Mugtord, S. C., and Castle, J. E., *Zeolites* **10**, 51 (1990).
10. Swift, P., Shuttleworth, D., and Seah, M. P., in "Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy" (D. Briggs and M. P. Seah, Eds.), p. 437. Wiley, New York, 1983.
11. Uwamino, Y., Ishizuka, T., and Yamatera, H., *J. Electron Spectrosc. Relat. Phenom.* **23**, 55 (1981).
12. Jones, R. A., and Bean, G. P. "The Chemistry of Pyrrole." Academic Press, London, 1977.
13. Breck, D. W., "Zeolite Molecular Sieves." Wiley-Interscience, New York, 1974.
14. Zalewski, D. J., Chu, P.-J., Tutunjian, P. N., and Lunsford, J., *Langmuir* **5**, 1026 (1989).
15. Borade, R. B., Adnot, A., and Kaliaguine, S., *J. Chem. Soc. Faraday Trans.* **86**, 3949 (1990).
16. Smith, G. F., *Adv. Heterocycl. Chem.* **2**, 287 (1963).
17. Pignataro, S., Dimarino, R., Distefano, and G., Mangini, A., *Chem. Phys. Lett.* **22**, 352 (1973).
18. Carlson, T. A., "Photoelectron and Auger Spectroscopy." Plenum, New York, 1975.
19. Borade, R., Sayari, A., Adnot, A., and Kaliaguine, S., *J. Phys. Chem.* **94**, 5989 (1990).