Base and acid sites in alkaline earth cation-exchanged X zeolites

J. Xie, M. Huang and S. Kaliaguine [1]

Département de Génie Chimique et CERPIC, Université Laval, Québec, Canada G1K 7P4

Received 16 June 1994; accepted 2 September 1994

Alkaline earth exchanged X zeolites are characterized by pyrrole chemisorption using FTIR spectroscopy. Lewis basic, Lewis acidic (cations) and also Brønsted acidic sites were detected in these zeolites. Based on a local environmental model, the charges on oxygens (basic sites) and cations are further calculated using the electronegativity equivalence method. The NH stretching frequencies of pyrrole chemisorbed on both basic and acidic sites are well correlated with these charges. This relationship supports the early idea that the alkaline earth cations in faujasite exist in the form of $(MOH)^{1+}$.

Keywords: pyrrole adsorption; FTIR; alkaline earth exchanged X zeolites; base and acid sites

1. Introduction

Acidity and basicity are paired concepts, which are often responsible for the catalytic properties of catalysts, specially zeolites. Over the past thirty years extensive studies have been devoted to the acid properties of zeolites because of their high activity and selectivity in petrochemical catalysis. In contrast, less attention has been paid to the characterization of their basic properties. Recently, the base sites of solid catalysts, specially of zeolites, and their catalytic behaviour have received growing attention [1–9]. In zeolites it is generally accepted that the base sites are the framework oxygens [2,6–8]. As discussed in several papers of our group [6,10], zeolite basicity is a rather local property, as the basic strength is mainly influenced by the local environment of the basic site. A local model was then suggested to calculate the negative charge on oxygens (basic sites) using the electronegativity equivalence method, and this charge was found to be well correlated with the infrared NH stretching frequency of pyrrole chemisorbed on basic sites. As proposed by several authors [2,6,11], the shift in NH stretching frequency of the pyrrole molecule is actually a measurement of the basic sites strength.

---

[1] To whom correspondence should be addressed.

As a probe molecule, pyrrole possesses various advantages [12]: its vapour pressure is convenient for studying adsorption from the vapour phase, the NH FTIR bands should not interfere with the OH bands of the adsorbents. Another important feature is probably its amphoteric character allowing it to interact with both basic (Lewis base) and acidic sites (Lewis and Brønsted acids) [6,7]. Generally, the adsorption of pyrrole on basic sites causes a relatively large bathochromic shift of its NH stretching frequency, because the hydrogen atom of the NH bond interacts directly with the basic sites. On the other hand, the adsorption on acid sites causes just a relatively small bathochromic shift in NH stretching frequency, because the acid sites interact with the pyrrole ring rather than the hydrogen atom of the pyrrole molecule. However, in most cases of alkali exchanged faujasites only the basic sites can be detected by chemisorbed pyrrole. This may be explained by the predominant adsorption of pyrrole on the relatively strong basic sites of these samples. A simultaneous detection of both Lewis basic and Lewis acid sites has been recently reported for a series of aluminophosphate molecular sieves [8]; however, the characteristic IR band of pyrrole for basic sites was very weak due to the lower density of basic sites in these samples.

Lewis basic sites and Lewis acid sites coexist in zeolite lattices. Therefore, for suitable relative values of base and acid strengths, simultaneous detection of these sites by pyrrole chemisorption should be possible. Suitable candidates for this kind of detection would be the alkaline earth exchanged faujasites, which possess weaker basicity compared with alkali exchanged faujasites. Moreover, early investigations revealed that Brønsted acid sites are also present in these zeolites [13]. Therefore, a series of alkaline earth cation exchanged X zeolites was prepared in this work. The pyrrole adsorption technique was further employed to characterize both the basicity and acidity of these samples. The results were correlated with the charges on basic and acidic sites, which were calculated from Sanderson electronegativities. Based on these results, the nature of both basic and acidic sites in alkaline earth exchanged X zeolites will be discussed in the present paper.

2. Experimental

Samples of NaX zeolite were exchanged with Ca, Sr and Ba cations from their chloride solutions to prepare CaX, SrX and BaX samples, while magnesium nitrate was used in ion exchange to prepare MgX zeolite. Each exchange lasted for 24 h at 80–85°C. Three successive exchanges were performed in order to obtain a high exchange level. After each ion exchange, the zeolite slurry was filtered and washed with 500 ml hot water (about 50–60°C) for three times, followed by drying at 120°C overnight. The unit-cell chemical compositions of all samples were determined by atomic absorption spectroscopy. The analysis results are shown in table 1.

For infrared experiments, zeolite samples were pressed into self-supported wafers (about 10 mg with $\varnothing = 1.3$ cm). These wafers were mounted in a pyrex

Table 1
Unit composition of alkaline earth exchanged zeolites

MgX-1	$Na_{28.8}Mg_{28.3}[(AlO_2)_{85.4}(SiO_2)_{106.6}]$
MgX-2	$Na_{24.0}Mg_{30.7}[(AlO_2)_{85.4}(SiO_2)_{106.6}]$
MgX-3	$Na_{22.0}Mg_{31.7}[(AlO_2)_{85.4}(SiO_2)_{106.6}]$
CaX	$Na_{1.4}Ca_{42.0}[(AlO_2)_{85.4}(SiO_2)_{106.6}]$
SrX	$Na_{1.8}Sr_{41.8}[(AlO_2)_{85.4}(SiO_2)_{106.6}]$
BaX	$Na_{1.4}Ba_{42.0}[(AlO_2)_{85.4}(SiO_2)_{106.6}]$

vacuum cell with calcium fluoride windows. The vacuum cell was designed to accommodate four different samples. The cell was then connected to a vacuum line and samples were degassed at 400°C overnight ($p = 10^{-4}$ Torr). After cooling to room temperature the samples were exposed to pyrrole vapour for 10 min followed by evacuation at different temperatures. The spectra were then recorded after every step of the treatment using a Digilab FTS-60 spectrometer with a 2 cm^{-1} resolution.

X-ray powder diffraction patterns were recorded using a Philips X-ray diffractometer with Cu Kα radiation (1.5405 Å) and a graphite monochromator.

3. Results and discussion

Before pyrrole adsorption, all the alkaline earth exchanged X zeolites displayed a weak and broad band around 3600 cm^{-1} after dehydration at 400°C (spectra not shown). The frequency and also the broad shape of the band suggest the presence of minor OH groups interacting with water molecules. In fact, a very weak band at 1630 cm^{-1} was also detected for these samples. After adsorption of pyrrole and subsequent evacuation at 65°C, a series of new bands appeared (fig. 1). In the high frequency region (2700–3760 cm^{-1}), seven bands were detected at 3300–3400 (strong and broad), 3130, 3114, 3090, 3060, 2947 and 2850 cm^{-1}. The bands around 3140 and 3105 cm^{-1} of liquid phase pyrrole were attributed [12] to the four CH stretching modes (every band used twice). The same assignment was then accepted here for the bands of 3130, 3114, 3090 and 3060 cm^{-1}. The appearance of four bands can be explained by the removal of band degeneracy after adsorption. The 2945 and 2850 cm^{-1} bands were described as combination bands and taken as a distinct indication of the presence of strong basic sites by several authors [2,3]. In our case, the 2945 cm^{-1} band is definitely present and the intensity of this band increased regularly in the order $Mg < Ca < Sr < Ba$. But the 2850 cm^{-1} band is not evident except for the BaX spectrum in which it is, however, quite weak. The strong and broad band around 3300–3400 cm^{-1} is usually attributed to the NH stretching vibration.

The main feature after pyrrole adsorption is certainly the strong and broad NH stretching band. Obviously, this band shifts to lower frequency in the order $Mg > Ca > Sr > Ba$. It is located at 3406, 3382, 3361 and 3331 cm^{-1}, respectively.

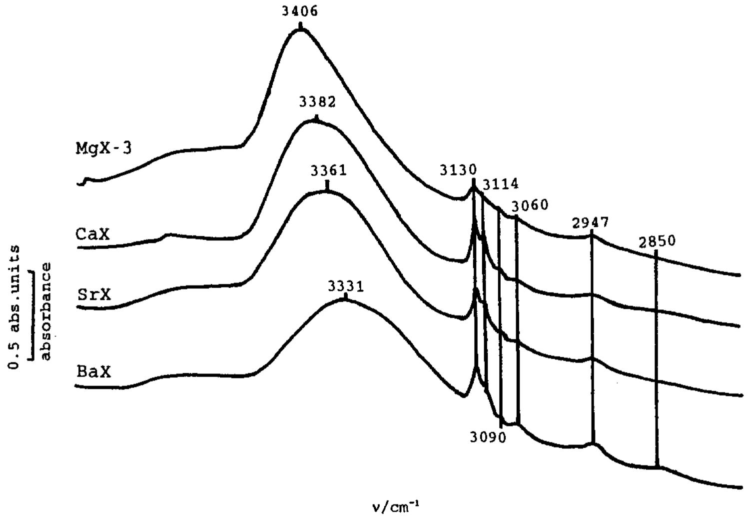


Fig. 1. High frequency region of IR spectra after pyrrole adsorption and following evacuation at 65°C.

The NH stretching band of the free pyrrole molecule in CCl_4 (3497 cm^{-1}) is sharp [11], while the NH stretching band observed in liquid pyrrole is broad owing to intermolecular association [12]. Here, in a solid system, a simple reason for the broad band could be the distribution of basic strength of adsorption sites [6,7]. For example, in our previous work of alkali exchanged X zeolite, the coexistence of two NH stretching bands for a zeolite containing two kinds of cations was established. In the present case, each zeolite contains also two kinds of cations: the alkaline earth cation and the residual sodium cation (table 1). Therefore, two peaks corresponding to two cations in the NH stretching region should be also present. In fact the coexistence of two bands can be directly observed in the case of MgX-1, which possesses the highest sodium content among a series of MgX zeolites (fig. 2). The 3280 cm^{-1} band appearing in MgX samples has the same position as that in NaX zeolite, therefore this band was attributed to pyrrole adsorbed on framework oxygens adjacent to sodium cations [6,7]. When the sodium content decreased in the order MgX-1 > MgX-2 > MgX-3, the intensity of the 3280 cm^{-1} band also decreased in the same order. A computer deconvolution was further performed for the NH bands for all these samples. The IR spectra in the region 3150–3500 cm^{-1} were submitted to a deconvolution operation which involves manipulation of Fourier transforms by triangular apodization using the following parameter values: half-width, 70–80 cm^{-1}; K-factor, 2.5–3 [14]. The results are shown in fig. 3. It is interesting to note that there are actually three bands in the NH stretching region for MgX, CaX, SrX and one broad band for BaX. Following the above argument, the weak and common band at 3280 cm^{-1} in the deconvolution spectra of MgX, CaX, and SrX samples was still attributed to pyrrole adsorbed on framework oxygen adjacent to sodium cations [6].

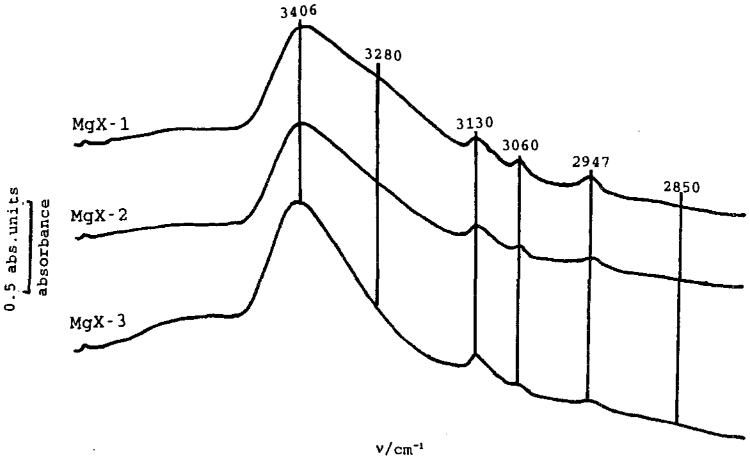


Fig. 2. High frequency region of IR spectra after pyrrole adsorption and following evacuation at 65°C for MgX with different exchange levels.

Fig. 4 shows the ring stretching region of IR spectra after pyrrole adsorption. A series of bands appeared at 1600, 1528, 1486, 1469, 1447, 1418, 1376 and 1286 cm^{-1}. The positions of all these bands are consistent with those observed for pyrrole chemisorbed on basic and/or acid zeolites. As pointed out in our previous work, the ring stretching bands of chemisorbed pyrrole provide an important indication for the nature of adsorption sites. The band around 1470 cm^{-1} indicates the presence of Lewis basic sites and/or physically adsorbed pyrrole, while the band around 1490 cm^{-1} indicates the presence of Lewis and/or Brønsted acid sites [6–8]. Since the physically adsorbed pyrrole can be removed by evacuation at 65°C, the detection of a band at 1469 cm^{-1} revealed the presence of Lewis basic sites over these samples (low in SrX and BaX). On the other hand, the appearance of the 1486 cm^{-1} band suggests the presence of acid sites. However, since both pro-

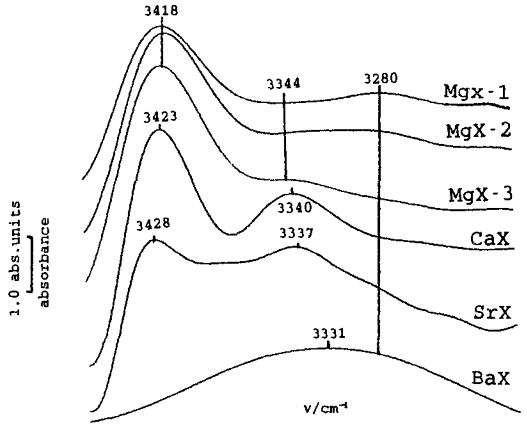


Fig. 3. Deconvolution of NH bands after pyrrole adsorption and following desorption at 65°C.

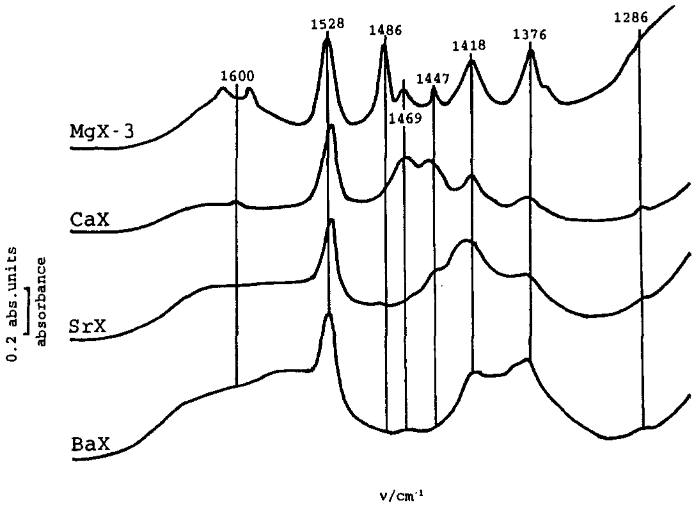


Fig. 4. Ring stretching frequency region of IR spectra after pyrrole adsorption and following evacuation at 65°C.

tons (the weak 3600 cm^{-1} band after dehydration) and cations exist in these samples, the nature of these acid sites cannot be cleared out. In order to obtain a direct comparison between the amounts of Brønsted and Lewis acid sites, pyridine adsorption was then performed on these samples. The corresponding IR spectra are shown in fig. 5. The weak band at 1542 cm^{-1} proved the presence of small amount of Brønsted acid sites, while the bands at 1441–1445 cm^{-1} are due to the pyridine species associated with Na, Mg, Ca, Sr and Ba cations. The molar extinction coefficient ratio between Lewis and Brønsted acid sites is 1.15 for chemisorbed

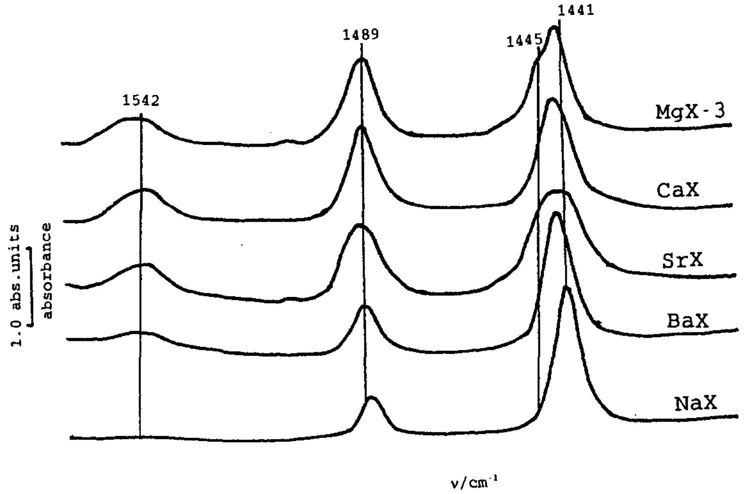


Fig. 5. IR spectra after pyridine adsorption and following evacuation at 120°C for 2 h.

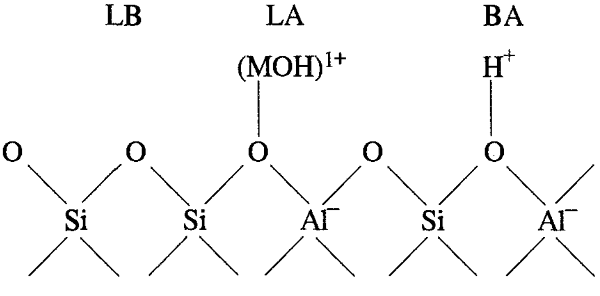
pyridine in the case of Y zeolite. A rough estimate using this ratio suggests that the amount of alkaline earth cations detected by pyridine adsorption is about twice as large as that of Brønsted acid sites.

The assignments of the bands obtained after deconvolution (fig. 3) are then as follows. The bands at 3344, 3340, 3337 and 3331 cm^{-1} in MgX, CaX, SrX and BaX, respectively, are still attributed to pyrrole adsorbed on Lewis basic sites, namely the framework oxygens adjacent to alkaline earth cations. The high frequency combined with the appearance of a 1486 cm^{-1} band (in the ring stretching region) indicates that the bands at 3418, 3423 and 3428 cm^{-1} are not due to pyrrole associated with basic sites but with acid sites. Moreover, as discussed above, these acid sites are mainly Lewis acid sites.

Previous work [6] revealed that the regular change in frequency of the NH stretching band of chemisorbed pyrrole can be explained using Sanderson's electronegativity. Since the cations in the supercage of faujasite are mainly located near the six oxygen ring [15], in the case of a divalent cation M, the local composition may be approximately taken as $Si_{6-n}Al_nO_{12}M_{n/2}$ around basic sites. The intermediate electronegativity for this hypothetical compound would be

$$S_{\mathrm{int}} = (S_{\mathrm{Si}}^{6-n} S_{\mathrm{Al}}^{n} S_{\mathrm{O}}^{12} S_{\mathrm{M}}^{n/2})^{1/(18+n/2)} .$$

The charge on oxygen was then calculated for the present samples and the results are correlated with the NH stretching frequency as shown in fig. 6a. Data previously observed for alkali exchanged X zeolite [6,7] are also shown in fig. 6a. Obviously, instead of the straight line drawn from the data of alkali exchanged X zeolites, a bend curve may extend to the data of alkaline earth exchanged X zeolites (solid circle). In other words, the strength of these basic sites measured by the NH stretching frequency is larger than that expected from the extrapolation of this linear relationship. However, it is generally accepted that a simple divalent cation cannot satisfy the charge distribution requirements of the zeolite lattice in the absence of water. During dehydration, the electrostatic field around an alkaline earth cation may induce dissociation of coordinated water molecules to produce $(MOH)^{1+}$ and H^{1+} species [13]. Accepting this explanation, the extraframework Lewis acid sites would not be M^{2+} but $(MOH)^{1+}$. Consequently the basic sites should be the framework oxygen adjacent to this cation. A model is then drawn as follows:



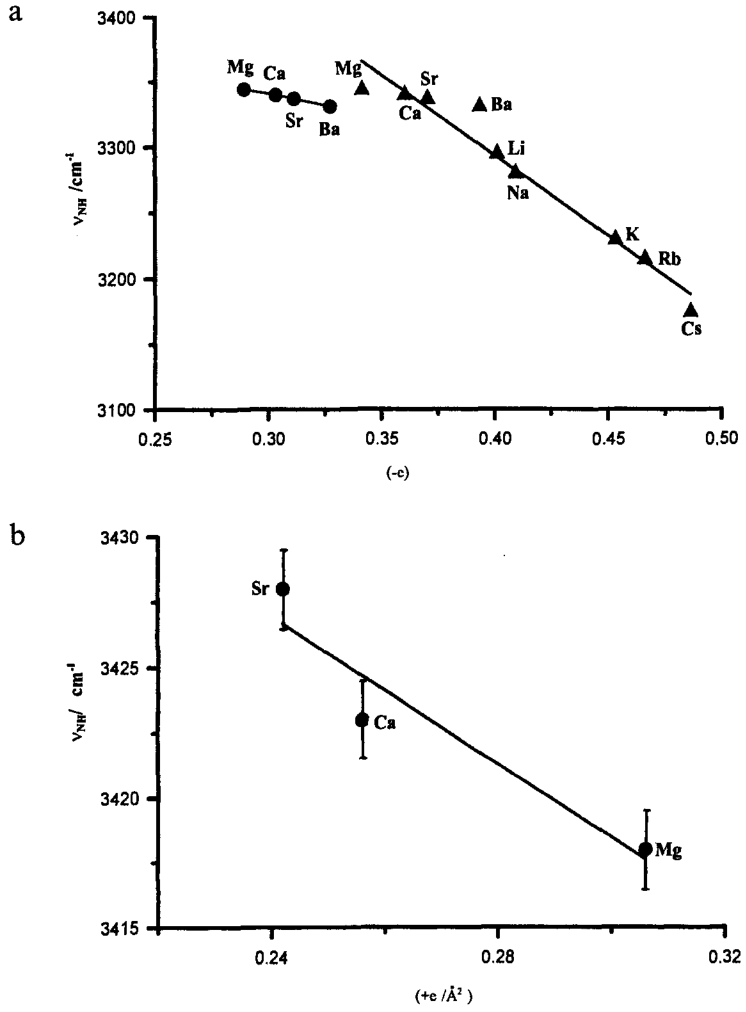


Fig. 6. (a) Relationship between the charges on oxygen and the NH wavenumber of pyrrole adsorbed on basic sites. The data of alkaline exchanged X zeolite were taken from ref. [6]. Solid circles for alkaline earth exchanged X zeolites are obtained after calculation using $Si_{6-n}Al_nO_{12}M_{n/2}$ as the local composition, while the solid triangles using $Si_{6-n}Al_nO_{12}(MOH)_n$ as the local composition. (b) Relationship between the charge on the metal atom divided by the square of atom radius and the NH wavenumber of pyrrole adsorbed on acid sites.

Based on this model, the local chemical composition around basic sites was represented as $Si_{6-n}Al_nO_{12}(MOH)_n$, and the intermediate electronegativity for this hypothetical compound as

$$S_{\mathrm{int}} = [S_{\mathrm{Si}}^{6-n} S_{\mathrm{Al}}^{n} S_{\mathrm{O}}^{12} S_{\mathrm{MOH}}^{n}]^{1/(18+3n)} ,$$

$$S_{\mathrm{MOH}} = (S_{\mathrm{M}} S_{\mathrm{O}} S_{\mathrm{H}}) .$$

Then, according to the electronegativity equivalence method (EEM) [16], the charges on oxygens were re-calculated, and the data were also reported in fig. 6a (solid triangles). The $(MOH)^{1+}$ cation may be regarded as a pseudo alkali cation. According to both Barthomeuf [2] and our previous work [6], there should be a linear relationship between the NH stretching frequency and the charge on the basic site (oxygens) in these alkali cation exchanged zeolites, provided the zeolites possess the same crystal structure. Fig. 6a shows that the fit of these solid triangles with the straight line is acceptable. Therefore, these data of pyrrole chemisorbed on basic sites seem to support the early idea according to which the cation is in the form of $(MOH)^+$ in alkaline earth-exchanged faujasites. This kind of cation should induce a stronger basicity on the adjacent oxygen as measured by the calculated electronic charge, than that expected from the bare divalent cation.

On the other hand, since the 3418, 3423 and 3428 cm^{-1} bands in MgX, CaX and SrX samples, respectively, are mainly due to pyrrole adsorbed on Lewis acid sites, these frequencies would be related to the charge on the cation group $(MOH)^{1+}$. One possibility is that, similar to the situation of Brønsted acid sites, the π electron of the pyrrole ring will interact with the hydrogen atom of the $(MOH)^{1+}$ group. However, the calculation indicated that the charge on this hydrogen atom is negative in the cases of CaX, SrX and BaX, and only slightly positive in the case of MgX. In other words, the OH group in $(MOH)^{1+}$ can be regarded as a Brønsted base group. As established in our previous work [6–8], Brønsted bases cannot be detected by chemisorption of the pyrrole molecule. Thus the other possibility is that the pyrrole ring still interacts with the metal atom of these cations. A steric factor must be taken into consideration in this case. It is noticed that the positive charges on these alkaline earth metal atoms calculated from the above model are around $+1\ e$ (0.78 (Mg), 0.99 (Ca), 1.12 (Sr) and 1.40 (Ba)), therefore the radii of these charged metal atoms should be larger than that of the corresponding divalent cation and smaller than that of the corresponding atom. If we approximately estimate the radii of these charged metal atoms using the following equation: $r = (r_{\mathrm{atom}} + r_{\mathrm{divalent\,cation}})/2$, thus the radii of these cations are around 1.3 Å, which is comparable with that of most transition metal atoms. The steric factor would then not create an additional barrier for the interaction between pyrrole and these alkaline earth metal atoms. Following our previous suggestion [17] the charge on the metal atom of this cation group was divided by the square of the metal atom radius, and the result was taken as a measurement of Lewis acidity. Its relationship with the NH stretching frequency is shown in fig. 6b. The correlation shows that the order of Lewis acidity is MgX > CaX > SrX, which is opposite to the one of NH stretching frequency.

A question still remains for the only one band observed with the BaX sample. This band (3331 cm^{-1}) is attributed to pyrrole adsorbed on basic sites due to its lower frequency (relatively large bathochromic shift in NH stretching frequency). In fact, the Sanderson electronegativity calculation also revealed that BaX possesses the stronger basicity among these samples. Therefore, the absence of a NH band corresponding to pyrrole adsorbed on acid sites may be also due to the weak

Lewis acid strength of the Ba cation and consequently the desorption of the corresponding pyrrole during evacuation at 65°C. Vice versa, an opposite example is provided by MgX samples, where the strong Lewis acidity caused a strong band at 3418 cm^{-1}, while the band corresponding to basic sites is weak. It is further noticed that the intensity of the only band in the BaX sample is also relatively weak, though the exchange level for the Ba cation is even higher than that of Mg cations in MgX. A reasonable explanation would be linked with different cation locations in these samples. Fig. 7 shows the X-ray powder diffraction (XRD) patterns for alkaline earth exchanged X zeolites. According to the empirical relationship suggested by Lunsford et al. [18,19], the cations are randomly distributed within the large cavities of faujasite, provided that the intensities of 331, 311, and 220 XRD peaks satisfy the relationship $I_{331} > /I_{220} > I_{311}$. Clearly, this is the case with MgX, CaX and SrX. On the other hand, if $I_{331} > I_{311} > I_{220}$, the cation will prefer to occupy other sites, such as I′ and II sites [18,19]. In the case of the BaX sample, we do observe the order $I_{311} > I_{220}$; however, the intensity of I_{331} is very low. Breck [15] has concluded that the strength of the electronic field around a cation is an important factor which determines its site population. A cation with high field strength will occupy the larger cavities, while a cation with low field strength will occupy the sites in small cages, such as the site I in hexagonal prism cages. The Ba cation should possess the lowest field strength among all the alkali earth cations. Combined with the XRD results, a certain portion of Ba cations will occupy the sites in small cages (β cage and hexagonal prism cage). Then the basic sites adjacent to these cations would not be approachable by pyrrole molecules due to the small window size. Therefore only a weak band intensity was observed.

In summary, infrared data for pyrrole adsorption on alkaline earth exchanged X zeolites are reported here. Lewis base, Lewis acid (cations) and also Brønsted acid sites coexist in these zeolites. The NH stretching frequencies of pyrrole

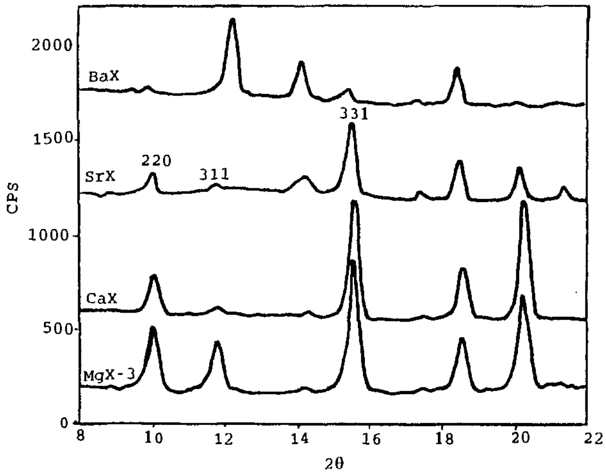


Fig. 7. X-ray powder diffraction patterns.

adsorbed on both basic and acidic sites are related with the charge on the oxygens and cations. This relationship does not contradict the early idea that the alkaline earth cations in faujasite exist in the form of $(MOH)^{1+}$. These cations would then be the Lewis acid sites in these zeolites, while the adjacent framework oxygens are the basic sites. Brønsted acid sites are also produced due to the dissociation of water, however, the portion of these Brønsted acid sites which can be detected by pyridine adsorption is relatively small.

References

[1] Y. Ono, Stud. Surf. Sci. Catal. 5 (1980) 9.
[2] D. Barthomeuf, J. Phys. Chem. 88 (1984) 42.
[3] D. Barthomeuf and A. de Mallmann, Stud. Surf. Sci. Catal. 37 (1987) 364.
[4] Y. Okamoto, M. Ogawa, A. Maezawa and T. Imanaka, J. Catal. 112 (1988) 427.
[5] P.E. Hathaway and M.E. Davis, J. Catal. 116 (1989) 263; 116 (1989) 272.
[6] M. Huang and S. Kaliaguine, J. Chem. Soc. Faraday Trans. 88 (1992) 751.
[7] M. Huang and S. Kaliaguine, Stud. Surf. Sci. Catal. 73 (1992) 291.
[8] D.B. Akolekar, M. Huang and S. Kaliaguine, Zeolite (1994), in press.
[9] M. Huang and S. Kaliaguine, Catal. Lett. 18 (1993) 373.
[10] M. Huang, A. Adnot and S. Kaliaguine, J. Am. Chem. Soc. 114 (1992) 1005.
[11] P.O. Scokart and P.G. Rouxhet, J. Chem. Soc. Faraday Trans. I 76 (1980) 1476.
[12] R.A. Jones and G.P. Bean, *The Chemistry of Pyrrole* (Academic Press, London, 1977).
[13] J.A. Rabo, *Zeolite Chemistry and Catalysis* (American Chemical Society, Washington, 1976).
[14] Fourier Manipulations (User's Manual), Bio-Rad Laboratories, Cambridge (1989).
[15] D.W. Breck, *Zeolite Molecular Sieves: Structure, Chemistry, and Use* (Wiley, New York, 1974).
[16] R.T. Sanderson, *Chemical Bonds and Bond Energy* (Academic Press, New York, 1976).
[17] M. Huang and S. Kaliaguine, Stud. Surf. Sci. Catal. 78 (1993) 559.
[18] W.H. Quayle and J.H. Lunsford, Inorg. Chem. 21 (1982) 97.
[19] M.B. Ward and J.H. Lunsford, in: *Proc. 6th Int. Zeolite Conf.*, Reno, 10–15 July 1983, p. 405.