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# NOTE

# Microcalorimetric Characterization of the Basicity in Alkali-Exchanged X Zeolites

The basicity of zeolites has been discussed by several authors (1–6). In general, the basic sites in zeolites are regarded as the framework oxygens. Basic strength and the density of basic sites decrease with an increase in framework Si/Al ratio, while basic strength increases with an increase in electropositivity of the countercation in zeolites. The use of pyrrole as an IR probe to determine the basicity in zeolites was first reported by Barthomeuf (2, 3). Following Barthomeuf's works, the characterization of chemisorbed pyrrole was extended using XPS (5) and a detailed observation in the IR ring stretching region (6) was also made. It was found that whenever the zeolite sample contains two kinds of alkali cations, two different $N_{1s}$ peaks in XPS and two different NH stretching vibration bands in IR are obtained, corresponding to pyrrole chemisorbed on these two sites. These results allowed us to conclude that the basic sites in alkali-exchanged faujasite are the framework oxygens adjacent to alkali cations, and the basicity is determined mainly by the local environment (7). It was also noted that, as an amphoteric molecule, adsorbed pyrrole can characterize both the basicity and acidity in zeolites (6). Since the Lewis base (the framework oxygen) and Lewis acid (the countercation) are conjugated to each other, then the distinction between the pyrrole species chemisorbed on basic and acid sites must be taken into account. Previous IR results (6) had revealed that pyrrole only adsorbed on the basic sites of alkali-exchanged X and Cs-exchanged Y zeolites, and no band corresponding to the adsorption of pyrrole on acid sites could be detected for these samples.

In this work the chemisorbed pyrrole on alkali-exchanged X zeolites was characterized using differential calorimetry. In fact, heat flow microcalorimetry (8) is one of the best methods known for measuring accurately the differential heats of adsorption and so yielding a thermodynamic scale for the energy distribution of surface sites. A series of alkali-exchanged X zeolites and also a Cs-exchanged Y sample were then examined by microcalorimetry using pyrrole as a probe. The details of the sample preparation had been reported previously (5, 6). Table 1 lists the unit-cell compositions of all these samples, established by atomic absorption spectrometry. The heats of adsorption were determined using a heat-flow microcalorimeter of the Tian–Calvet type (C80 from Setaram), linked to a volumetric line that permitted the introduction of a small dose of gaseous pyrrole. The equilibrium pressure after every adsorption was measured by means of a differential pressure gauge (Datametrics). Successive doses were sent onto the sample until a final equilibrium pressure of 0.5 Torr was obtained. Adsorption isotherms and heats of adsorption were then determined simultaneously. Before adsorption the samples were evacuated at 673 K overnight. In order to calculate the irreversibly chemisorbed amount ($V_{\text{irr}}$), the sample was pumped at 338 K at the end of the first adsorption, and a second adsoprtion was then performed at the same temperature. $V_{\text{irr}}$ was determined by the difference between the primary and secondary isotherms. The differential heats of adsorption were also measured during acquisition of the second isotherm. These ranged between 75 and 95 kJ/mol, which are still definitely higher than the heat of pyrrole liquefaction (41.67 kJ/mol at 353 K) (9). Therefore the irreversibly adsorbed pyrrole ($V_{\text{irr}}$), which is still more strongly adsorbed, is entirely chemisorbed pyrrole. The calorimetric and volumetric data were stored and analyzed by microcomputer processing. The adsorption temperature was maintained at 338 K. The previous IR results (6) confirmed that physisorbed pyrrole was removed after evacuation ($10^{-5}$ Torr) at this temperature.

Figure 1 represents the differential heat of adsorption for each sample at 338 K versus the adsorbed volume. All the curves of differential heat of adsorption as a function of the amount adsorbed are similar in shape. At the very beginning a sharp decrease in $Q_{\text{diff}}$ is generally observed, which should be assigned to the adsorption on a few very strong sites. In the next region a relatively slight decrease or plateau in $Q_{\text{diff}}$ is observed, corresponding to the heats released during adsorption on the predominant sites. Finally, the evolved heat falls drastically into the physisorption domain. Careful analysis indicated that the region of slow decrease of the curves usually contains two plateaus. The two plateaus or two regions of slow decrease are very

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## TABLE 1

Unit-Cell Composition of Zeolite Samples

| | |
|---|---|
| LiX | $Li_{54.3}Na_{31.1}(AlO_2)_{85.4}(SiO_2)_{106.6}$ |
| NaX | $Na_{85.4}(AlO_2)_{85.4}(SiO_2)_{106.6}$ |
| KX | $K_{48.3}Na_{37.1}(AlO_2)_{85.4}(SiO_2)_{106.6}$ |
| RbX | $Rb_{37.7}Na_{47.7}(AlO_2)_{85.4}(SiO_2)_{106.6}$ |
| CsX | $Cs_{28.8}Na_{56.6}(AlO_2)_{85.4}(SiO_2)_{106.6}$ |
| CsY | $Cs_{37.0}Na_{17.5}(AlO_2)_{54.5}(SiO_2)_{137.5}$ |

apparent in the case of CsX. The $Q_{diff}$ for the first plateau of CsX is centered at 146 kJ/mol while it is 117 kJ/mol for the second plateau. A region of relatively fast decrease in $Q_{diff}$ is observed between the two plateaus. The two plateaus can be also distinguished in the cases of RbX, KX, LiX, and CsY. However, in the case of NaX, only one region of slow decrease is observed. The *dn/dQ* versus $Q_{diff}$ curves were then extracted from these data. Clearly, corresponding to the presence of two plateaus in Fig. 1, there are two peaks or two maximum values in Fig. 2 for LiX, KX, RbX, CsX, and CsY samples, and only one peak for the NaX sample. The $Q_{diff}$ responsible for the maximum of *dn/dQ* is referred to $Q_{max}$. It is found that the first $Q_{max}$ values for KX, RbX, and CsX samples is nearly the same as that of NaX (around 117 kJ/mol). The only $Q_{max}$ for NaX should be the differential heat characteristic of the strength of basic sites associated with Na cations. The appearance of the same $Q_{max}$ then suggests the existence of the same basic sites associated with Na cations for KX, RbX, and CsX samples. This is reasonable since all three samples still contain significant amounts of Na cations (see Table 1). Consequently, the second $Q_{max}$ observed in KX, RbX, and CsX samples should correspond to the differential heat characteristic of the strength of basic sites associ-

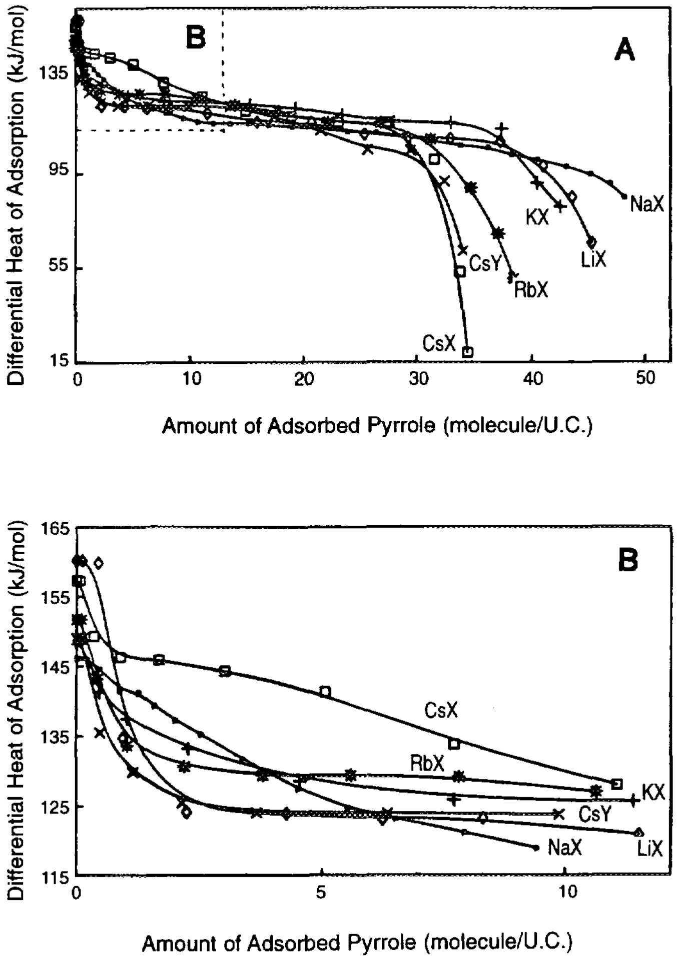

FIG. 1. Differential heat of pyrrole adsorption versus the adsorbed volume.

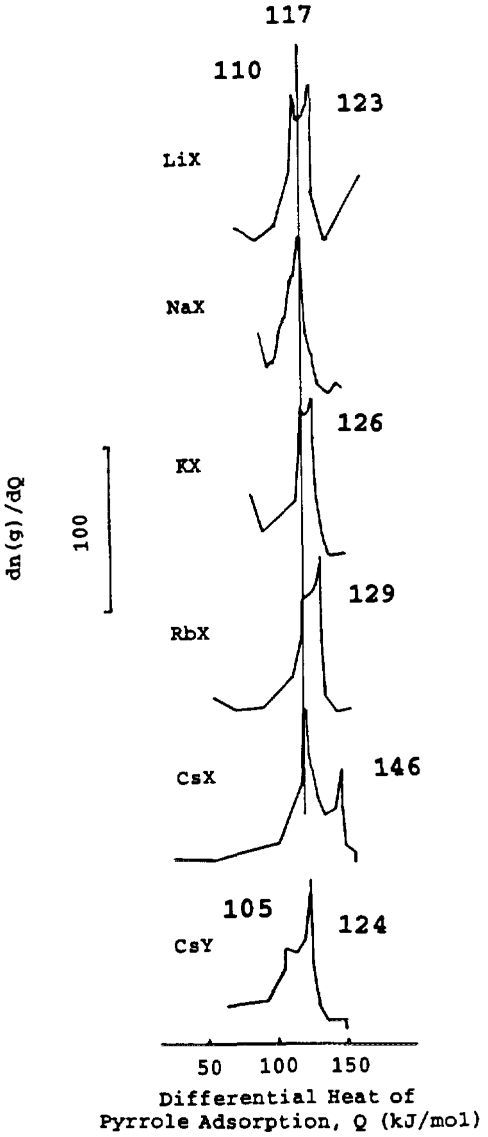

FIG. 2. *dn/dQ* versus the differential heat of pyrrole adsorption.

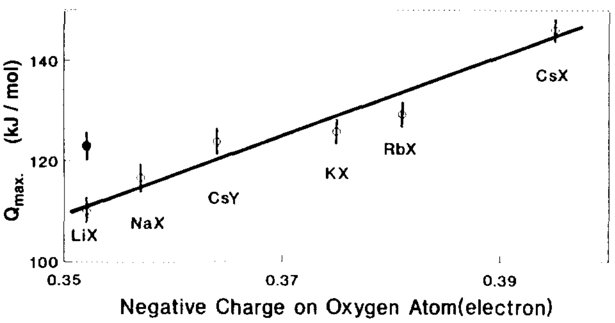

FIG. 3. Relationship between the negative charge on oxygen and $Q_{max}$ of chemisorbed pyrrole. ⧫ denotes the second peak of LiX in Fig. 2.

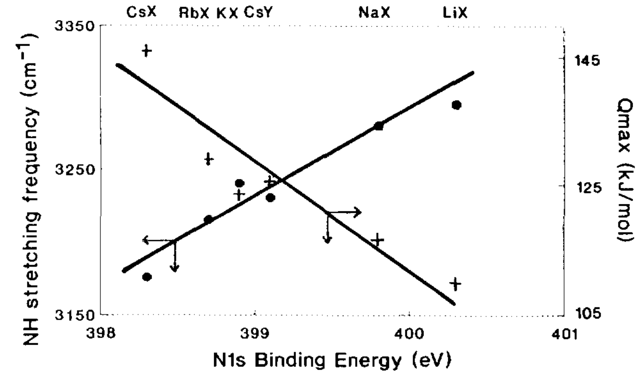

FIG. 4. Relationship between $N_{1s}$ binding energies, NH stretching frequencies, and $Q_{max}$ of chemisorbed pyrrole.

ated with other kinds of cations, the K, Rb, and Cs cations, respectively. Therefore, consistent with IR (6) and XPS (5) results, the calorimetric titration also revealed the coexistence of basic sites with two different strengths, which are associated with the two different cations.

The CsY sample also includes two kinds of cations (Table 1); the change in *dn/dQ* also displays two maximum values. Since the basic site associated with the Cs cation should possess a stronger base strength, the $Q_{max}$ with a high value (124 kJ/mol) for CsY is assigned to the differential heat characteristic of the basic sites associated with Cs cations, while the $Q_{max}$ of 105 kJ/mol is characteristic of basic sites associated with Na cations in Y zeolite.

The situation of LiX is different. The first $Q_{max}$ at 110 kJ/mol may correspond to the basic sites associated with Li cations in X zeolite; however, the second $Q_{max}$ at 123 kJ/mol is too high to correspond to the basic sites associated with Na cations in X zeolite (117 kJ/mol). The base strength in zeolites can also be expressed by the negative charges on oxygens (2, 6), which are calculated from the Sanderson electronegativity equivalence method (6, 10). The $Q_{max}$ corresponding to different cations (first $Q_{max}$ for LiX and NaX, second $Q_{max}$ for KX, RbX, CsX, and CsY) are then plotted versus these charges and shown in Fig. 3. Clearly, there is a good relationship between the charges and the characteristic $Q_{max}$. The second $Q_{max}$ of the LiX sample is also drawn in Fig. 3 (the solid point). It deviates from the straight line. A possible assignment for this second $Q_{max}$ is a combination contribution from different sites. A part of this contribution still comes from the basic sites associated with Na cations (located around 117 kJ/mol), and another part could be due to the adsorption on another kind of site. The Li cation possesses the highest charge/radius ratio among alkali cations and will produce a strong polarizing effect. Depending on the local structural environment of a cation site (type of zeolite oxygen ring: 4R, 6R ..., nature and distribution of the closest atoms, and so on), this strong polarizing effect of the Li cation may produce a contraction of the T–O–T angles of the zeolite framework around some of the siting of the $Li^+$ cation. According to Barthomeuf (3), this contraction effect may lead to an increase in the basicity of the associated oxygens. This would be in line with our observation of a The $Q_{max}$ value of 123 kJ/mol, which is 6 kJ/mol higher than the value associated with $Na^+$ in the NaX sample.

As mentioned earlier, the same samples were previously examined by XPS and FTIR (5, 6). The coexistence of two $N_{1s}$ peaks in XPS and two NH-stretching bands in IR was also observed, provided the sample contains two kinds of alkali cations. Figure 4 compares the characteristic parameters of chemisorbed pyrrole measured by different methods, namely the $Q_{max}$, the $N_{1s}$ binding energy, and the NH-stretching frequency. Clearly, there are good correlations between each pair of these parameters. This is consistent with the model of pyrrole chemisorbed on the basic site (5): there is a bonding between the framework oxygen (Lewis basic site) and the H atom of the NH group of the pyrrole molecule. The stronger base will produce a larger heat of adsorption, a transfer of electrons from a basic site to a nitrogen atom of a NH group, and then a lower $N_{1s}$ binding energy; moreover, a looser NH bonding resulted in a lower NH stretching frequency.

Table 2 summarizes the thermodynamic results cited

TABLE 2

Thermodynamic Results of Pyrrole Adsorption at 65°C

| Sample | $V_{irr}$ (Molecule/u.c.) | $Q_{int.irr}/V_{irr}$ (kJ/mol) | $Q_{init}$ (kJ/mol) | $Q_{max}$ (kJ/mol) | |
|---|---|---|---|---|---|
| | | | | 1st | 2nd |
| LiX | 35.9 | 118 | 160 | 110 | 123 |
| NaX | 40.8 | 116 | 146 | 117 | |
| KX | 35.2 | 121 | 148 | 117 | 125 |
| RbX | 28.3 | 123 | 152 | 117 | 129 |
| CsX | 22.5 | 129 | 157 | 117 | 146 |
| CsY | 23.7 | 122 | 149 | 105 | 124 |

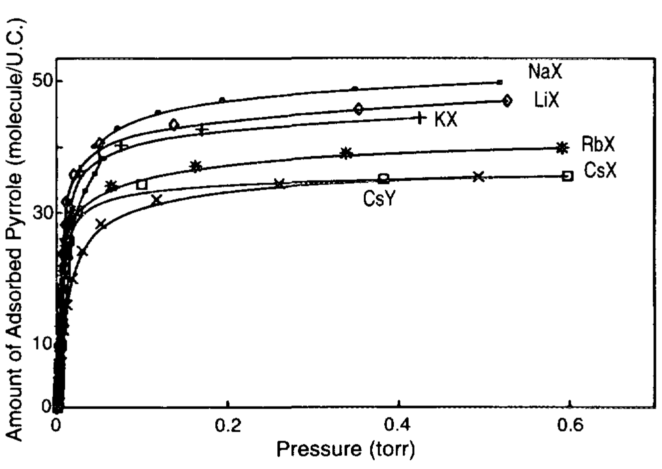

FIG. 5. Volumetric isotherms of pyrrole adsorption at 338 K.

above. The irreversibly adsorbed volumes of pyrrole are consistent with the previous gravimetric adsorption measurements (5) and correspond to about four pyrrole molecules in every supercage. The difference in $V_{irr}$ depending on different cations is also obvious. This difference can be even observed directly from the adsorption isotherms (Fig. 5). In general, $V_{irr}$ decreases with an increase in the cation size. However, once again, the LiX sample is different; it possesses a $V_{irr}$ smaller than expected from its small cation size. As mentioned above, this may be attributed to the distortion of the framework due to the strong polarizing effect of Li cations. The low $V_{irr}$ value observed with the LiX sample may also be reflecting the partial hydroxylation of $Li^+$ cations, yielding LiOH species which would not adsorb pyrrole.

In brief, a thermodynamic scale of the Lewis basic strength distribution of alkali-exchanged X zeolites is obtained by heat flow microcalorimetry using pyrrole as a probe. From this result further evidence is yielded to support our previous conclusion: the Lewis basicity in alkali-exchanged zeolites is a local property, strongly influenced by the adjacent alkali cation.

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