Characterization of Acid Sites in Pentasil Zeolites by X-Ray Photoelectron Spectroscopy

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The N_{1s} XPS band of pyridine chemisorbed on Al-ZSM-5 zeolite was found to be properly deconvoluted into three component peaks. In a previous contribution these three components were assigned to pyridine chemisorbed on two kinds of Brønsted acid sites and one Lewis acid site. This analysis is extended here to Fe-ZSM-5 and B-ZSM-5. Isomorphous substitution of Fe for Si or Al in the zeolite framework leads to a slight decrease in the binding energy of the N_{1s} Lewis component. In the case of B substitution a decrease in the binding energy of all three N_{1s} components is observed. © 1990 Academic Press, Inc.

The Brønsted acid sites responsible for many catalytic reactions over ZSM-5 zeolites are known to be bridged hydroxy groups, $M(OH)Si$ (where M stands for Al, Fe, B, etc.). These bridged hydroxy groups give rise to a characteristic IR OH stretching band. The position of this band has been shown to vary with the framework substituent element (*1*, *2*).

In this report deconvolution of the N_{1s} XPS band of chemisorbed pyridine is performed for Al-ZSM-5, Fe-ZSM-5, and B-ZSM-5 zeolites. It is found that the N_{1s} envelope is composed of three subcomponents, and isomorphous substitution by B is shown to decrease the binding energy of all N_{1s} components.

Al-ZSM-5 was obtained by the procedure described by Gabelica *et al.* (*3*). B-ZSM-5 was synthesized according to the procedure of Howden (*4*). The synthesis of Fe-ZSM-5 was similar to that described in Ref. (*5*). To remove organic template, as synthesized zeolites were calcined at 500°C for about 15 h. These calcined samples were then repeated by ion exchange with 1 *M* ammonium nitrate solution. The protonated forms were obtained by calcining ammonium forms at

450°C in air for about 16 h. The residual sodium content in all samples as determined by atomic adsorption was less than 0.02%. Prior to pyridine adsorption at room temperature, zeolite activation was carried out at 400°C in a conventional high-vacuum system for about 16 h. Then the physisorbed pyridine was desorbed at room temperature by evacuation ($P = 10^{-5}$ Torr) for about 16 h.

The XPS spectra of all samples were recorded at room temperature using a V.G. Scientific Escalab Mark II system with a hemispherical analyzer operated at 20 eV. A Mg$K\alpha$ X-ray source ($h\nu = 1253.6$ eV) was used. The spectrometer was operated at 20 mA and 15 kV. The residual gas pressure in the spectrometer chamber during data acquisition was less than 10^{-7} Torr. The measurements were performed in the following sequence: Si_{2p}, N_{1s}, O_{1s}, $Al_{2p}/Fe_{2p}/B_{1s}$, and Si_{2p}. A binding energy of 103.3 eV for the Si_{2p} level was used as an internal reference for all samples. The accuracy of the binding energy as determined with respect to this standard value was within ±0.2 eV.

The intensity of various XPS bands was determined using linear background subtraction and integration of peak areas. N_{1s} peaks were deconvoluted into three compo-

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TABLE 1

Bulk and Surface Characteristics of *M*-ZSM-5 Samples

Sample	$(Si/M^a)_b$	$(Si/M)_s$	$(N/M)_s$
Al-ZSM-5(A)	45.9	47.4	1.07
Al-ZSM-5(B)	39.0	37.2	0.92
Fe-ZSM-5(C)	15.0	12.3	0.52
B-ZSM-5(D)		59.0	1.15

^{a} *M* stands for Al, Fe, or B for respective samples.

nents by keeping full width at half maximum (FWHM = 2.4 ± 0.1 eV) constant for all components and assuming that each peak has Gaussian–Lorenzian shape (G/L range 0 to 20%).

Ratios of the atomic concentrations in outer surface layers of the samples were estimated from the corresponding XPS peak area ratios using the relation

$$\left(\frac{X}{M}\right)_s = \frac{A_x}{A_M} \cdot \frac{\sigma_M}{\sigma_x} \cdot \frac{\lambda_M}{\lambda_x} \sqrt{\frac{E_{Kx}}{E_{KM}}},$$

where *X* stands for silicon or nitrogen and *M* for aluminum, iron, or boron; and *A*, σ, λ, E_K are the normalized peak area, the effective ionization cross section, the escape depth, and the photoelectron kinetic energy, respectively. Cross section values determined by Scofield (6) and escape depths calculated from the formulas given by Vulli and Starke (7) are employed here.

The chemical composition expressed by the bulk atomic ratio $(Si/M)_b$, the surface atomic ratios $(Si/M)_s$, and $(N/M)_s$ calculated from XPS intensity ratios of the samples studied are given in Table 1. If we assume that each *M* species is associated with either one Brønsted or one Lewis acid sites and each site adsorbs one pyridine molecule then one should expect $(N/M)_s = 1$. The $(N/m)_s$ ratio for Al-ZSM-5 and B-ZSM-5 samples is quite close to one indicating that Al or B species present in the zeolites are associated with either Brønsted or Lewis acid sites. In the case of Fe-ZSM-5 zeolite, the $(N/Fe)_s$ ratio is significantly lower than

one which suggests that this sample contains nonacidic extra-lattice oxidic iron species. The presence of extra-lattice oxidic iron species has been confirmed by the appearance of a shoulder peak to the main O_{1s} XPS peak (Fig. 1C). The main peak due to zeolite lattice oxygen appears at 532.6 eV and a shoulder peak corresponding to oxygen associated with extra-lattice oxidic iron species appears at 530.1 eV (8, 9). Figure 2 shows the Fe_{2p} spectrum of Fe-ZSM-5 (sample C). This spectrum displays only few, if any, interferences from the Auger line of oxygen, O_{KVV}.

The binding energy and FWHM values of various components present in zeolites are given in Table 2. Both the BE and FWHM values of Si_{2p}, Al_{2p}, and O_{1s} levels in our samples agree well with those reported in the literature (10, 11). The remarkable feature of Table 2 is that N_{1s} peaks are substan-
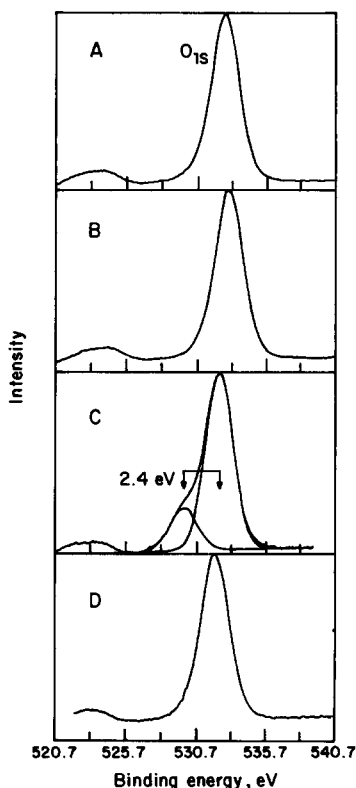

FIG. 1. O_{1s} XPS spectra of *M*-ZSM-5 zeolites.

TABLE 2

Binding Energy and FWHM Values of Various Components Present in M-ZSM-5 Samples

Sample	Si_{2p}		M^a		O_{1s}		N_{1s}	
	BE^b	$FWHM^b$	BE	FWHM	BE	FWHM	BE	FWHM
A	103.3	2.4	74.5	2.4	532.9	2.4	399.5	3.3
B	103.3	2.4	74.8	2.5	533.1	2.4	400.2	4.6
C	103.3	2.3	710.6	2.4	532.5	2.4	400.0	3.6
D	103.3	2.3	192.6	2.5	532.1	2.4	399.6	4.6

^{a} M stands for Al_{2p}, $Fe_{2p3/2}$, or B_{1s} levels for corresponding samples.
^{b} BE and FWHM values are in eV.

tially broader and less symmetric (see Fig. 3) than those of Si_{2p}, Al_{2p}, and O_{1s} peaks. Similar kind of observations have been made by Defosse and Canesson (12) who studied the N_{1s} XPS spectra of adsorbed pyridine on NH_4Y zeolites activated at various temperature. The FWHM value of N_{1s} peaks were about 5 eV. They attributed this broadening of the N_{1s} peak to a distribution of acidity over a wide range of acid strengths. Therefore, it is considered that the N_{1s} peak is actually a composite peak that must be deconvoluted.

In Fig. 3 the deconvoluted N_{1s} XPS peak for the samples of Table 1 is illustrated. For all samples except Fe-ZSM-5 zeolite, deconvolution of N_{1s} XPS spectra into two components resulted in peaks having FWHM value of 2.8 ± 0.1 eV. As all other elements with singlet XPS line show peaks

with FWHM of 2.4 ± 0.1 eV we believe that this 2.8-eV value is not acceptable. We have, however, found that three peaks with FWHM = 2.4 ± 0.1 eV are resolvable for
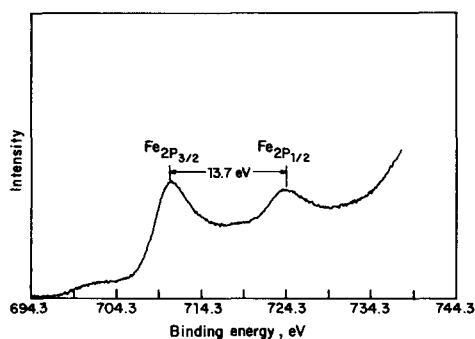

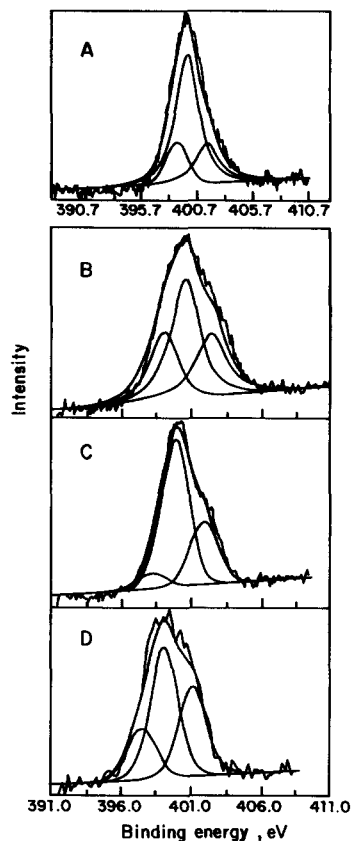FIG. 2. Fe_{2p} XPS spectra of Fe-ZSM-5.

FIG. 3. N_{1s} XPS spectra of pyridine chemisorbed on samples of Table 1.

all samples. In the case of Fe-ZSM-5 zeolite, N_{1s} peak can be deconvoluted into two as well as three components with FWHM of 2.4 eV because the contribution of a third component is very small (Fig. 3C). It is therefore considered that this sample contains a negligible amount of Lewis acid sites on its surface. Recent studies (8) performed in our laboratory using a curve fitting of the N_{1s} XPS envelope of pyridine chemisorbed on Al-ZSM-5 zeolite with different Si/Al ratios indicated that there exist three N_{1s} components corresponding to binding energy values of 398.7, 400.0, 401.8 eV. The respective peaks were assigned to the pyridine associated with Lewis acid sites and pyridinium ions bonded with relatively weak and strong Brønsted acid sites. The peak assignments are further supported by the fact that the Brønsted to Lewis ratio determined by this method for samples with uniform spatial distribution of Al is in good agreement with the one derived from IR absorbance ratios.

The $(B/L)_{IR}$ ratio was determined from IR absorbance ratios as follow. Prior to pyridine adsorption at room temperature for 15 min, samples were activated at 400°C for about 16 h under vacuum (10^{-5} Torr) and then degassed at 200°C (Al-ZSM-5 and Fe-ZSM-5) or 100°C (B-ZSM-5) for about 16 h under vacuum (10^{-5} Torr). The sample spectra were recorded at room temperature using a Digilab FTS-60 spectrometer. The IR bands at 1545 and 1455 cm^{-1} assigned to pyridinium ions and coordinatively bound pyridine, respectively, were used to determine the relative concentrations of Brønsted and Lewis sites. This ratio was determined by using the relation

$$\frac{B}{L} = \frac{A_B}{A_L} \cdot (\varepsilon_L/\varepsilon_B),$$

where A_B/A_L stands for IR absorbance ratio and $(\varepsilon_L/\varepsilon_B)$ is the extinction coefficient ratio. The $(\varepsilon_L/\varepsilon_B)$ for ZSM-5 zeolites is taken as 1.5 (14).

The close agreement between $(B/L)_{xps}$ and $(B/L)_{IR}$ values supports our peak assignments. The large difference in the $(B/L)_{xps}$

TABLE 3

Binding Energy of N_{1s} Components and Brønsted to Lewis Ratios Determined by XPS and IR

Sample	Binding energy, eV			B/L	
	(1)	(2)	(3)	XPS	IR
A	398.7	399.8	401.6	4.6	4.7
B	398.7	400.0	402.0	3.1	3.7
C	398.1	399.7	401.8	9.9	1.7
D	397.6	399.0	401.3	3.9	2.7[a]

[a] B/L value determined at pyridine desorption temperature 100°C.

and $(B/L)_{IR}$ values observed for Fe-ZSM-5 zeolite is not surprising since this sample contains extraframework material. Small variation in the $(B/L)_{xps}$ and $(B/L)_{IR}$ values for B-ZSM-5 zeolites seems to suggest that pyridine desorption temperature is an important factor in determining $(B/L)_{IR}$ ratio. For example, desorption of pyridine at 200°C from B-ZSM-5 zeolite resulted in the disappearance of pyridine Lewis band in the IR spectra. Here, it is important to mention that evacuation at room temperature for about 16 h ($P = 10^{-5}$ Torr) did not remove completely physisorbed pyridine from these samples (presence of pyridine band 1439 cm^{-1} in the IR spectra). But our XPS data showed (8, 15) that (N/Al)$_s$ as well as (B/L)$_{xps}$ ratios did not vary significantly when pyridine desorption from Al-containing zeolites was carried out in the temperature range of 25 to 200°C in a conventional high-vacuum system ($P = 10^{-5}$ Torr). This clearly shows that from these samples physisorbed pyridine does get desorbed at room temperature, at least from XPS-analyzed layers, when samples are evacuated in the XPS chamber at a pressure of 10^{-7} to 10^{-8} Torr.

Table 3 shows that isomorphous substitution by Fe leads to a slight decrease in the binding energy of the N_{1s} component associated with Lewis acid sites. The binding energy of N_{1s} components bonded with weak and strong Brønsted acid sites remains,

however, more or less the same as for Al-ZSM-5. A significant decrease in the binding energy is observed when boron is the substituent element. The shift in the binding energy toward lower values suggests that not only Brønsted but also Lewis acid sites in B-ZSM-5 are much weaker than those in Al-ZSM-5 or Fe-ZSM-5 zeolites. The relative binding energy is found to decrease according to Al-ZSM-5 $\geq$ Fe-ZSM-5 > B-ZSM-5. This order is consistent with the proposed acid strength of Al(OH)Si $\geq$ Fe(OH)Si > B(OH)Si groups in pentasil zeolites, as determined by IR and TPD studies (*1, 16, 17*).

In conclusion, N_{1s} XPS spectra are found to be made up of three components, each presumably corresponding to a unique acidity range. Fe-ZSM-5 prepared by isomorphous substitution is characterized by a decrease in binding energy of N_{1s} Lewis components and B-ZSM-5 by a decrease in binding energy of all N_{1s} components, as compared to the Al-ZSM-5 zeolite.

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