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The XPS Study of Modified Y Zeolites[1]

Recently transition metal cation exchanged zeolites have been studied (*1*) by X-ray photoelectron spectroscopy (XPS). Using XPS, Vedrine *et al.* (*2*) found Pd(I) formation in PdY zeolite on reduction with hydrogen. Similarly, the formation of Rh(I) in RhY zeolite as a stable intermediate during the reducton of Rh(III) to Rh^0 by heat treatment in vacuum has been detected by XPS (*3*). XPS has been used to investigate (*4, 5*) the external layers of some zeolite surfaces. We have investigated the external surface composition of ferric exchanged Y zeolites with respect to percent exchange and thermal treatment by XPS.

EXPERIMENTAL

Ferric exchanged Y zeolites were prepared by treating Linde NaY with aqueous solutions of ferric acetate–acetic acid at about 4 pH at 27–30°C (*6*). Sodium and ferric contents were determined by flame photometry and atomic absorption spectrometry respectively. The spectra were recorded on an ESCA-III Vacuum Generator Spectrometer. The exciting radiation was Al$K\alpha$ with an energy of 1486.6 eV. The spectral resolution of the analyzer was ~1.0 eV. The binding energy of the electrons was determined within ±0.2 eV and reproducibility is checked. The pressure in the analyzer chamber was 10^{-8} Torr. Au $4f_{7/2}$ (83.8 eV) was used as a standard along with C 1*s* (285.0 eV). The powdered catalyst was pressed on gold-mesh and heated at 200°C for 1 h in the preparation chamber.

RESULTS AND DISCUSSION

During the process of ferric ion exchange, dealumination of zeolite did not occur (*6*) and the bulk silicon/aluminum ratio designated by $(Si/Al)_B$ for all the samples was 2.37 (determined by chemical analysis) (*6*). The Si/Al composition of the external layers in NaY and FeNaY zeolites were determined from the relative intensities of 2*s* peaks in the XPS using the following equation,

$$\frac{I_1}{I_2} = \frac{n_1}{n_2} \cdot \frac{\sigma_1}{\sigma_2} \cdot \frac{\lambda_1}{\lambda_2} \cdot \frac{S_1}{S_2}$$

$$= \frac{n_1}{n_2} \cdot \frac{\sigma_1}{\sigma_2} \cdot (T_{1,2}),$$

where

I = area under the curve (including satellites if present),
n = atomic concentration of the element,
σ = effective ionisation cross section,
λ = mean free path of the photoelectrons of kinetic energy E_c,
S = transmission factor of the spectrometer for an energy E_c.

For the given elements, the ratio $((\sigma_1/\sigma_2) \cdot T_{1,2})$ is called as the relative spectrometer intensity factor. (σ_1/σ_2) is taken as 1.27 (*7*).

The (Si/Al) ratios for the zeolite samples investigated by XPS are given in Table 1. The ratio denoted by $(Si/Al)_S$ refers to the composition of the external surface of the samples. The $(Si/Al)_S$ ratios are higher than $(Si/Al)_B$ and show a small increase with the percentage ferric exchange. This indicates that the external zeolite surface is aluminum deficient. Tempere *et al.* (*4*) reported surface (Si/Al) ratios obtained by XPS and found aluminum deficient external surfaces of A, X, and Y zeolites.

In order to examine the effect of thermal activation, FeNaY (82) was heated at 500°C for 5 h in air and is designated as FeNaY

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TABLE 1

Bulk and External Surface (Si/Al) Composition of Zeolites

Zeolite	$(Si/Al)_{2s}$ XPS area ratio	$(Si/Al)_{surf-}$ by XPS	$(Si/Al)_{bulk}$ gm. atom ratio by chemical analysis
NaY	4.94	3.89	2.37
FeNaY (46)[a]	5.08	4.00	2.37
FeNaY (82)	5.69	4.48	2.37
FeNaY (82, 500, 5)	3.18	2.51	2.37

[a] The figure in parentheses indicates percentage ferric exchange.

(82, 500, 5). The X-ray diffractogram confirms the crystallinity of the sample (*6*). The surface $(Si/Al)_S$ ratio of FeNaY (82, 500, 5) by XPS was found to decrease due to thermal treatment from 4.48 to 2.51 as given in Table 1. The thermal treatment of FeNaY (82) may cause dehydroxylation of the framework hydroxyl groups and simultaneous dealumination. The framework dehydroxylation of FeNaY has been reported in our thermogravimetric studies (*6*). The (bulk) aluminum migrates to the external surface thereby decreasing the surface $(Si/Al)_S$ ratio. Kerr (*8*) has discussed the mechanism of dealumination of zeolites. The present XPS results may be a novel extension of the conclusions of Kerr, indicating the thermal dealumination of the strongly hydroxylated framework.

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