Study of Brønsted acidity of NaHY zeolite by positron spectroscopy

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Angular correlations of positron annihilation gammas were applied to study NaHY zeolite catalysts whose acidity was altered by an ion-exchange process. The Brønsted acidity was found to vary linearly with the lineshape parameter of the angular correlation spectrum of the sample.

Keywords: acidity; positron annihilation; zeolite

1. Introduction

Zeolite catalysts are widely used in a large sector of the chemical industry for the purpose of promoting reaction rates. In particular, for petrochemical applications, such as cracking, dewaxing, and isomerization processes, etc. the outcomes crucially depend upon the activity of the selected catalysts to be used. The catalytic process is, however, rather complicated, and the detailed knowledge of the activity mechanism is still inadequate at best. Nevertheless, it is generally accepted that for zeolite catalysts, the surface acidity plays a vital role in their activities [1]. Yet, conventional methods for studying internal surfaces of catalytic materials are often far from being satisfactory, and new techniques for surface characterization are often desirable for contributing additional information about their surface acidity. In our earlier investigations [2–4] of catalytic materials, an unconventional, in situ technique (positron annihilation spectroscopy) for studying the Brønsted acidity of zeolites used for catalysts production was introduced and applied with remarkable success.

Positron annihilation spectroscopy (PAS) proves to be a powerful tool for studying electronic structures of solids. It has been applied to a wide range of materials, e.g., from metals to polymers (see, for example, ref. [5]). Its application to catalytic materials is, however, relatively rare and its potential for applications in this field is only initially explored [6]. Earlier work by Cheng et al. [7], and Nakanishi and Ujihara [8] involved PAS studies of porous materials, and primarily used positron lifetime measurements. The technique for acidity studies presented in this report represents a new application of the two-dimensional angular correlation of the annihilation radiation (2D-ACAR) spectrum of positrons annihilating in the zeolites under study. Positrons, after entering the sample material, always annihilate with electrons in the sample, resulting in an angular distribution of the annihilation radiation (ACAR). Two-dimensional ACAR was used for this experiment because of its excellent resolution and economy of time for data acquisition. The ACAR spectrum is generally a broad gaussian shaped curve. Some of the incident positrons would diffuse through the crystalline bulk and form positronium atoms (Ps) on the internal surfaces of the zeolitic catalyst, where acid sites reside. The final collapse of positronium atoms creates a distinctively much narrower gamma peak superimposing on the broad gaussian spectrum. The Ps population would be, however, reduced by the presence of protonic Brønsted acid sites through the oxidation of Ps atoms formed on the internal surfaces of the sample,

$$\mathrm{H}^+ + \mathrm{Ps} \rightarrow \mathrm{e}^+ + \mathrm{H} \qquad (1)$$

The appearance of Brønsted acid sites thus alters the over-all shape of the 2D-ACAR spectrum (see ref. [3]). A lineshape parameter S, defined as the percentage of the central area of the total spectrum area [3], is used to monitor the shape of the 2D-ACAR spectral line, and hence to gauge the variation of surface acidity of the sample. In this paper, we report results of 2D-ACAR studies of NaHY zeolite samples whose acidities were varied by the extent of NH_4^+ ion exchange.

2. Experimental

The experimental process involved in this study consists of preparing a series of ammonium sodium Y zeolite ($\mathrm{NH}_4^+\mathrm{NaY}$) samples by applying the conventional ion-exchange method, and measuring the 2D-ACAR spectra. A thermogravimetric analysis (TGA) was performed and an infrared (IR) absorption spectrum measured for each of the samples.

All of the samples of $\mathrm{NH}_4^+\mathrm{NaY}$ zeolites with various contents of NH_4^+ were prepared from a common parent sodium Y zeolite (supplied by PQ Corporation) containing 10.12% of Na by weight and a SiO_2/Al_2O_3 ratio of 5.0. Batches of the sodium Y zeolites were ion-exchanged with ammonium nitrate solutions at room temperature with varying length of time so as to yield products containing different concentrations of ammonium ions. Details of the ion-exchange process [8] are described in the steps 1–3.

Step 1: NaY zeolite, ammonium nitrate, and deionized water were mixed in a 1 : 1 : 10 weight ratio in a sealed bottle, and stirred at room temperature for 4 h.

Step 2: After a single 4 h ion exchange, the product was washed free of all soluble salts by using deionized water, and then dried at 100°C to become a powder. Part of this powder sample was used to repeat steps 1 and 2 to obtain a higher exchange ratio. Some of the product from step 2 was reserved for the TGA and IR analysis.

Step 3: Part of the sample materials obtained from step 2 were calcined at 420°C [9] for 4 h to decompose ammonium via

$$NH_4^+NaY \rightarrow NH_3 + NaH^+Y \qquad (2)$$

The product from step 3 was then ready for use in 2D-ACAR spectrum measurements.

The NaHY zeolite sample powder of about 0.1 g from step 3 was then pressed to form a disk of about 13.6 mm in diameter and 0.9 mm in thickness. The disk was exposed directly to positrons from a radioactive Na-22 source in a vacuum chamber maintained at 5×10^{-6} Torr at room temperature during measurement. A lineshape parameter S is evaluated for the 2D-ACAR spectrum of each sample. Details of the experimental arrangement are further described in ref. [3].

3. Results and discussion

Each sample with a different degree of ion exchange completed was subject to TGA analysis. For temperatures below 200°C a rapid weight loss was observed, which indicates the release of water molecules physically adsorbed on the sample. Another distinctive weight loss region occurred in the 200–400°C area, which signifies the escape of NH_3 from the crystal structure, leaving behind increased protonic Brønsted acid sites.

Fig. 1 shows a typical relative weight loss (by TGA) curve as a function of length of time for ion exchange (i.e. the number of batch exchanges) for NaY samples. After the initial few hours the weight loss rate became increasingly smaller, which is understandable considering that the strongly hydrated in-going NH_4^+ cations are prevented from diffusing into small cavities and narrow channels of the zeolite structure where the residual Na^+ ions may reside. The NH_4^+ ion-exchanged NaHY zeolites with various surface H^+ concentrations were further investigated by IR absorption spectroscopy.

Fig. 2 shows the difference IR absorption spectra in the 3200–3800 cm^{-1} region for four samples numbered 1 through 4 with sample 1 having the shortest ion-exchange duration and sample 4 the longest. The difference of IR spectrum between each sample and sample 1 is illustrated in the figure. The peaks at about 3500 and 3640 cm^{-1} signify the bonds for the hydroxyl groups [10]. Their intensities increase noticeably as the sample is more ion exchanged, thus providing a strong evidence that NH_4^+–Na^+ ion exchange for NaY results in producing protonic Brønsted acid sites as indicated by eq. (2).

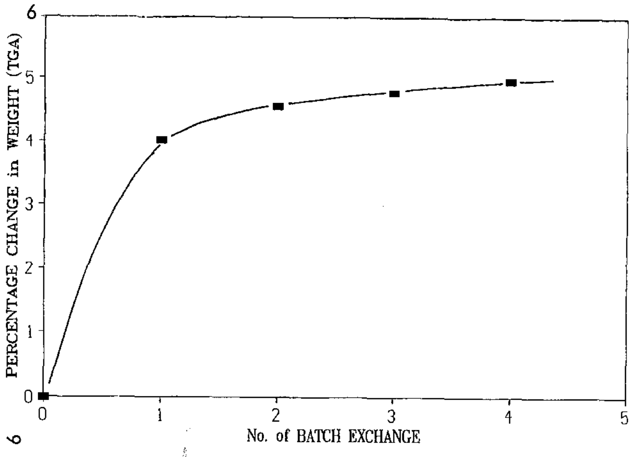

Fig. 1. Percentage weight loss vs. time for ion exchange. The solid line is arbitrarily drawn.

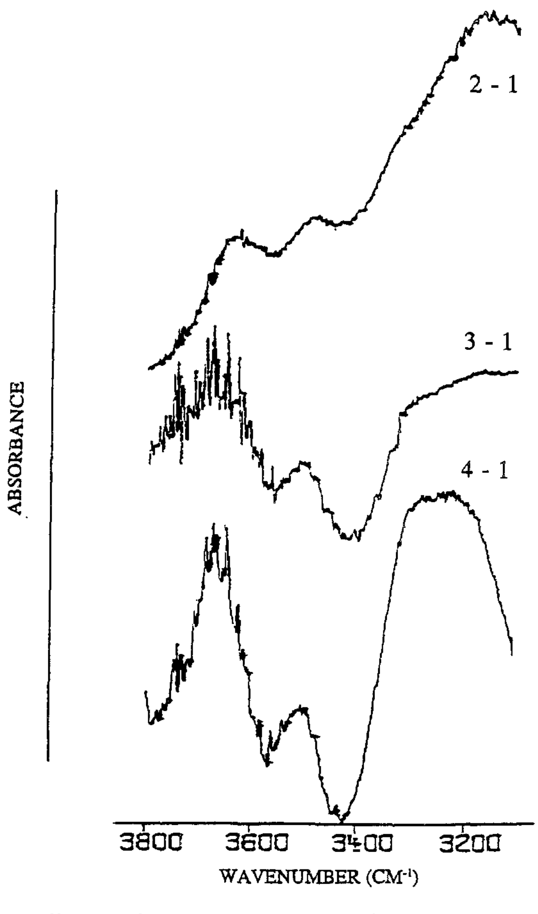

Fig. 2. Difference of IR spectrum between each sample and sample 1.

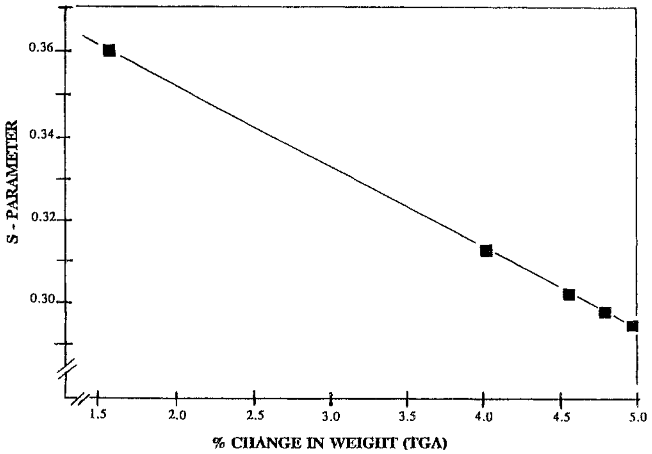

Fig. 3. A plot of lineshape parameter S and percentage of ion exchange (or Brønsted acid sites). The solid line is for guiding the eye.

Since H^+ sites tend to oxidize positronium atoms and thus reduce the Ps population, the lineshape parameter S of the 2D-ACAR spectrum would decrease as more NH_4^+–Na^+ ion exchange takes place.

Fig. 3 shows a monotonic dependence of the parameter S on the degree of ion exchange performed. The decrease in S values corresponds to increasing protonic acidity in the sample. The result thus illustrates the validity and effectiveness of this 2D-ACAR technique for detecting the change in Brønsted acidity of zeolite.

We have also investigated the possible effect of other cations on the lineshape measurements, which may be competing the oxidation of Ps atoms by protons. A set of NaY samples (PQ Corporation) with various Na contents but with like Si/Al ratios were tested in a similar experimental arrangement. Fig. 4 displays the response of the parameter S to the Na_2O content of the sample; little effect was observed as expected owing to the large difference in reduction potential between H^+ and Na^+ ions.

The Si/Al ratio of the framework of zeolites would also alter the acidity of the sample. As Si/Al ratio increases, more Brønsted sites are converted to Lewis sites which do not interact with Ps atoms. Conversely, the smaller Si/Al ratio value indicates a relatively larger number of Brønsted sites in the sample which would decrease the Ps population and thus reduces the S values as discussed above. A separate set of NaY samples (PQ Corporation) which have similar Na contents, but different Si/Al values, were analyzed by the 2D-ACAR spectroscopy. Fig. 5 shows that the measured values of lineshape parameter S indeed increase with the corresponding increase in Si/Al ratio of the samples.

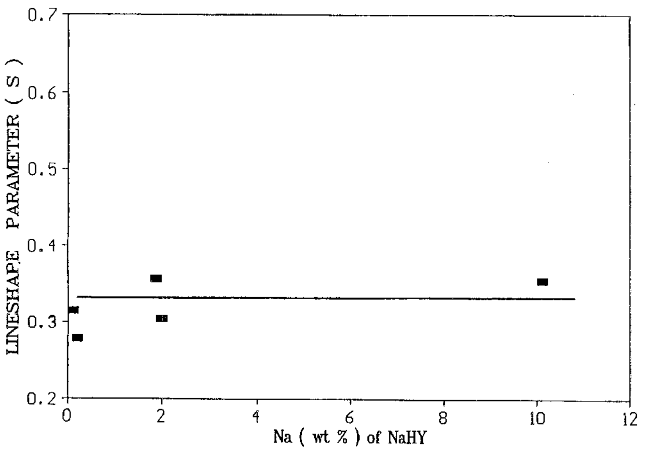

Fig. 4. A plot of lineshape parameter S vs. Na content in the sample. The solid line is for guiding the eye.

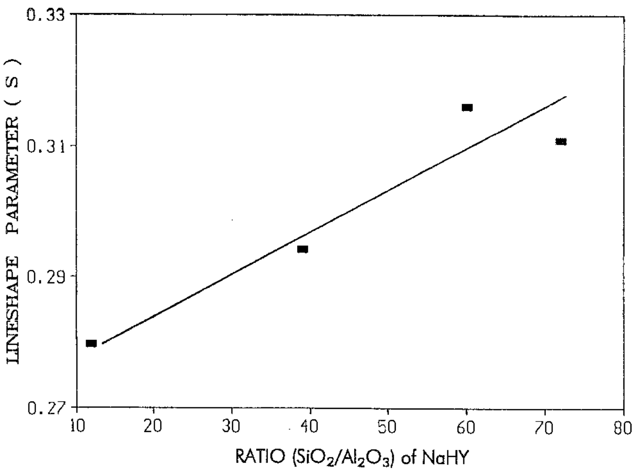

Fig. 5. A plot of lineshape parameter S vs. SiO_2/Al_2O_3 ratio in NaHY samples. The solid line is for guiding the eye.

4. Conclusion

In summary, this investigation has demonstrated the correlation between the lineshape parameter S of the positron annihilation spectrum and the Brønsted acid sites of zeolites. Owing to the fact that this technique monitors only the Brønsted acid sites situated on the surface which relates to the catalytic activity, there is little ambiguity about the location of the source of information obtained. This study has demonstrated the effect of ion exchange on surface acidity of Y zeolite and the uniqueness of positron spectroscopy for studying catalytic materials.

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