Brønsted acidic strength in Y-zeolite by positron spectroscopy

W.F. Huang [a], K.J. Hung [a], D.C. Huang [b], C.C. Huang [c] and P.K. Tseng [d]

[a] *Department of Physics, University of Louisville, Louisville, KY 40292, USA*
[b] *United Catalysts Inc., Louisville, KY 40292, USA*
[c] *Department of Physics, National Taiwan University, Taipei, Taiwan*
[d] *Department of Physics, Tam Kang University, Taipei, Taiwan*

Received 27 November 1998; accepted 25 March 1999

Angular correlation spectra of positron annihilation in Y-zeolite adsorbed with bases (ammonia, water, and alcohol) were studied. Results by the technique successfully reveal that there exist two types of Brønsted acid sites with different acidic strengths which require temperature of desorption of the base at about 200 and 400 °C.

Keywords: positrons, acidic strength, ammonia, water, alcohol, Y-zeolite

1. Introduction

Adsorption of bases is a widely used method to characterize surface acidity on solid catalysts [1,2]. The amount of acidity and acid strength distribution of surface acid sites in catalysts have been known to play a crucial role in promoting chemical reaction rates. Some adsorbates, especially NH_3 and water, are particularly useful probe molecules to study the surface acidity of zeolite catalysts with almost all cage sizes. Owing to the diminutive size of these bases, they can penetrate through the aperture of zeolite cages and interact there with the surface acid sites in the cages. This characterization method has been instrumental in explaining the activity and selectivity of zeolite catalysts in reactions where the reactant molecules can go through the channels of the zeolites.

The adsorption method combined with conventional analysis techniques, such as infrared spectroscopy (IR) [3–7], nuclear magnetic resonance (NMR) [8,9], X-ray photoemission spectroscopy (XPS) [10] and temperature-programmed desorption (TPD) [11,12], etc., have been extensively applied for the purpose of measuring the strength and the number, two independently distinguishable properties, of the Brønsted acid sites of surface OH groups in zeolites. In spite of their wide applications, each of the methods mentioned contains certain limitations in their applications to zeolite catalysts. For complex molecular systems such as zeolitic catalysts, the application of a single investigative method is often inadequate; only a combination of multiple experimental techniques may yield convincing results. The application of innovative techniques that may yield new perspectives and interpretations is therefore a very desirable segment of research in the study of such uniquely structured material as zeolites.

In this paper, we report results of investigation on distribution of Brønsted acidic strengths of NaHY by studying base-adsorbed zeolite samples using positron annihilation spectroscopy (PAS) which include measurements of positron lifetime in the sample and angular correlation of the annihilation radiation (ACAR). PAS has been applied in studies of electronic and morphological properties of a great variety of solid materials, including metals, semiconductors, and polymers, etc. [13]. The application of ACAR for zeolitic substances in characterizing physical and chemical properties of their internal surfaces, e.g., surface acidity, however, was attempted only recently [14,15], and its remarkable success has already pointed out an area where PAS is potentially capable to make a contribution.

Upon entering microporous polycrystalline solid materials such as zeolites, the incident positrons thermalize rapidly, and some of the positrons would annihilate with valence and core electrons in the bulk, generating two gammas propagating in opposite directions. The angular correlation of the annihilation radiation (ACAR) distribution, which basically is a measurement of momentum distribution of the electrons participating in the annihilation process, displays in general a broad Gaussian shape. A certain portion of the incident positrons, however, would diffuse through the polycrystalline bulk and appear on the internal surfaces of the pores and form with electrons there a hydrogen like bound atomic system called positroniums (Ps). The Ps atoms will eventually collapse and annihilate into two gammas whose ACAR spectrum is, nonetheless, distinguishably narrower than the one from the bulk. The overall ACAR spectrum of microporous samples such as zeolites is, therefore, in general composed of a central narrow peak superimposing on a broad Gaussian [16]. In the presence of protonic acidic sites (H^+) on the surface, the Ps atoms could be oxidized and its population decimated, thus reducing the central peak intensity and altering the overall ACAR spectrum. A lineshape parameter S defined as the ratio of the central area to the total area of the ACAR spectrum is customarily used to monitor changes of the ACAR spectrum. The plot of lineshape parameter S vs. specific

Brønsted acidity is therefore expected to be a linearly decreasing line.

The unique morphology of zeolites enables them to contain cages and channels which harbor OH groups with H^+ sites of possibly different strengths on their internal surfaces. Earlier work on application of PAS for zeolitic materials have demonstrated that lineshape parameter S of the ACAR spectrum responses sensitively with surface area and Brønsted acidity [14–16], whereas it is non-responsive to Lewis acidity.

PAS has proven to be a new and effective technique for monitoring specific Brønsted acidity of internal surfaces in materials such as zeolites. The PAS technique has the unique property that the information-carrying annihilation gammas are generated directly *in situ* on acid sites, eliminating possible uncertainties of identification of the origin of signals obtained. It is capable of yielding information about the sample under study that may not be readily feasible for other conventional methods. The technique also has the exclusive sensitivity to Brønsted acid sites, not affected by the Lewis sites. The information generated from PAS measurements is, therefore, conclusively descriptive of the Brønsted acid sites, not the combined acidity of both the Brønsted and Lewis sites. In this report we present results from investigating acidic strengths of the Brønsted acid sites in NaHY by applying the ACAR technique to zeolite samples adsorbed with different bases.

2. Experimental

The experimental process involved in this study comprises preparing water, alcohol, and ammonia adsorbed on NaHY zeolites, and *in situ* measurements of the ACAR spectra with a temperature-controlled sample chamber system [17]. All of the absorbed samples were prepared from the same NaHY prepared by using a conventional ion exchange method with ammonium salt, resulting in NH_4^+NaY zeolite which were then heated at 420 °C for about 4 h to decompose the NH_4^+ into NH_3 and H^+. Vapors of H_2O and alcohol (C_2H_5OH) were carried over by dry N_2 gas to the NaHY zeolite to form base-adsorbed Y-zeolite samples. A detailed description of the preparation of the base-adsorbed Y-zeolites is given in [17].

In situ measurements of the 2D-ACAR spectra with a temperature-controlled sample chamber were carried out to characterize the internal surfaces of the zeolite samples adsorbed with NH_3, H_2O and C_2H_5OH. About 0.1 g each of the powder sample was used to form a disk of about 13.6 mm in diameter and 1 mm in thickness. The disk was exposed directly to positrons from a radioactive Na-22 source in the sample chamber which was maintained at 5×10^{-6} Torr at room temperature during measurements. The incident positrons with an energy distribution following that of a beta decay are capable of penetrating and sampling various depths of the material under study. All heat treatments of samples were processed in the vacuum chamber [17]. A lineshape parameter S of the 2D-ACAR spectrum was evaluated for each heat-treated sample. In addition, a two-Gaussian fitting process [18] was applied to analyze the 2D-ACAR spectra to calculate the Ps peak intensities for the purpose of comparing results from S parameter evaluation of the samples after the desorption of base to uncover acid sites at a certain temperature.

3. Results and discussion

The lineshape parameter S values from 2D-ACAR spectra of the NaHY zeolite samples adsorbed with ammonia, water, and alcohol were measured as a function of desorption temperatures (figures 1–3). For water- and alcohol-adsorbed samples, at temperatures below 200 °C, an increase in S parameter indicates the release of physically

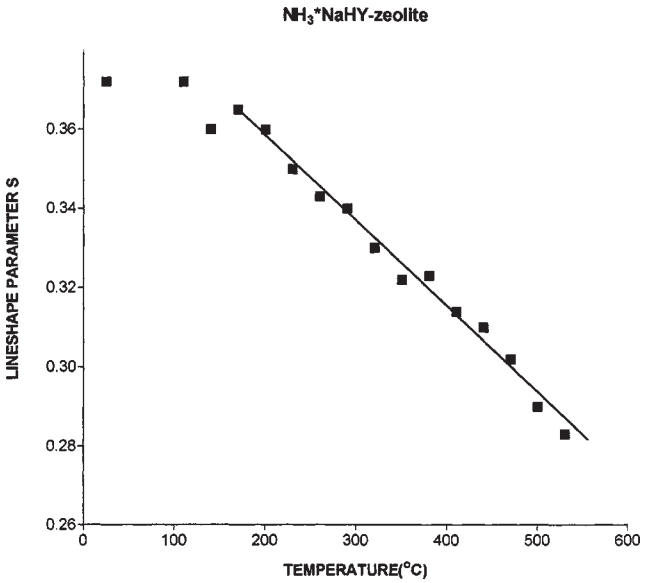

Figure 1. Lineshape parameter S vs. temperature for NH_3*NaHY zeolite. Solid line is arbitrarily drawn.

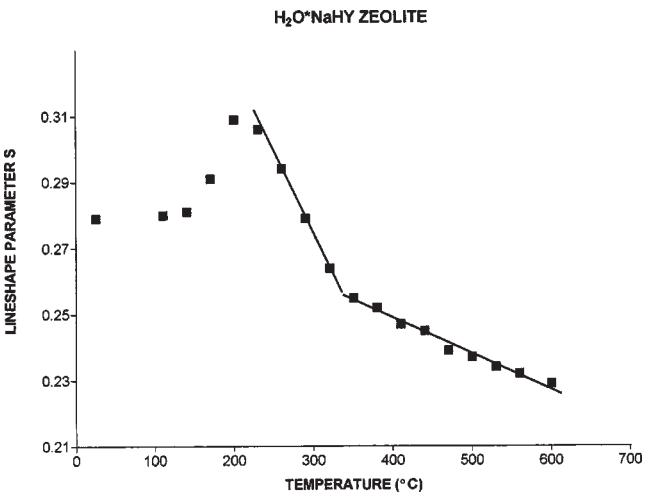

Figure 2. Lineshape parameter S vs. temperature for H_2O*NaHY zeolite. Solid line is arbitrarily drawn.

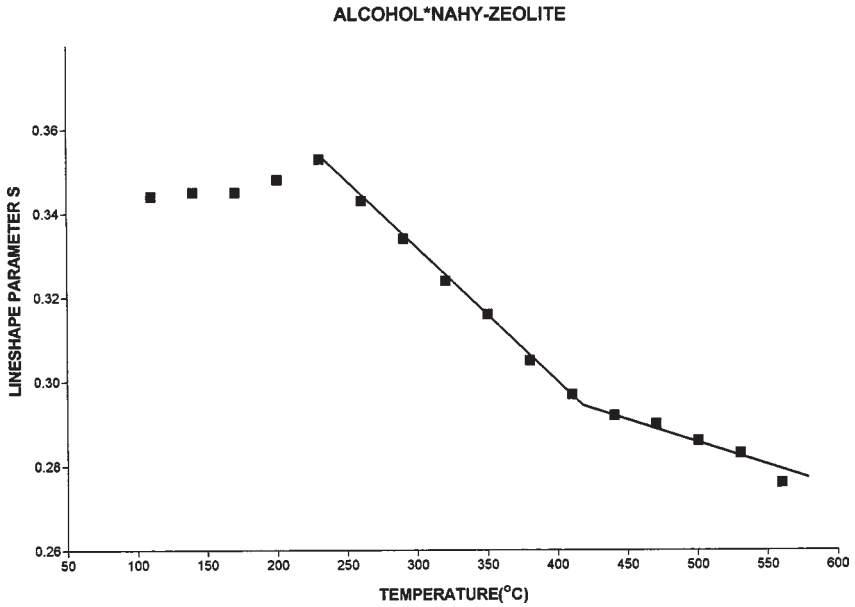

Figure 3. Lineshape parameter S vs. temperature for alcohol*NaHY zeolite. Solid line is arbitrarily drawn.

adsorbed water molecules. This process enhances the probability of positronium formation by increasing available surface area in the sample [13]. At temperatures higher than 200 °C, the decreasing S parameter is a result of base–acid decomposition which generates additional Brønsted acid sites and consequently reduces the positronium population and thus the S values. Of particular interest is the fact that the S parameter curve for H_2O*NaHY zeolite exhibits two regions with distinctively different slopes, one starts at 200 °C and the other at about 350 °C. The same characteristics of two slopes was also clearly present in the S parameter vs. temperature curve for alcohol-adsorbed NaHY zeolites with only different relative S values at 200 and about 400 °C. The feature of two slopes is a clear indication of the existence of two types H^+ sites with different acidic strengths. However, in the results of the ammonia-adsorbed sample no two-slopes feature was found.

Among the three adsorbates studied, ammonia, water, and alcohol, ammonia is the strongest adsorbed base, and alcohol the weakest. Strong base interacts with Brønsted acid sites of all strengths, while weaker base reacts preferentially the stronger Brønsted sites. Our results indicate that the S parameter probes not only the strong Brønsted acid sites but the weak ones as well. For the purpose of comparing results from the evaluation of S parameters, we have also analyzed the ACAR data by fitting a two-Gaussian curve [18]. The intensity of the central narrow Gaussian corresponds to positronium population. The plot of the positronium peak intensity as a function of the temperature of heat treatment of all three base-adsorbed samples are practically identical to the ones from using S parameter, with "two-sloped" features in temperatures higher than 200 °C for H_2O- and alcohol-adsorbed samples. As an example, figure 4 shows the plot of Ps peak intensity vs. temperature for H_2O-adsorbed NaHY zeolite. It thus reinforces the validity of the S parameter and provides further confirmation of the existence of the "two-slopes" feature in the desorption curves of water- and alcohol-adsorbed zeolites. The fact that the ammonia-adsorbed NaHY zeolite data did not exhibit the two-slopes feature is consistent with TPD results which show that there is no prominent second peak in the temperature range studied [19]. This observation also agrees with results from study of Brønsted acidity in zeolites by other researchers that ammonium ions are highly mobile and move in the crystalline sample in a very flat potential [20]. Their decomposition into ammonia molecules and protons could take place independently of OH bonds.

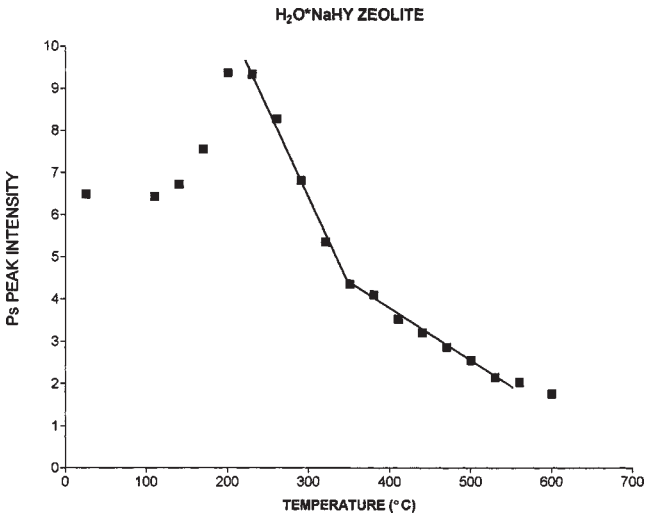

Figure 4. Positronium (Ps) intensity vs. temperature for H_2O*NaHY zeolite. Solid line is arbitrarily drawn.

4. Conclusions

Our results of study on base-adsorbed NaHY zeolites by using a new technique of ACAR measurements of the

PSA have evidenced the existence of two types of H^+ sites of different acid strengths. It further ascertains that ACAR of the PAS is an effective and valid technique for studying internal surface Brønsted acidity, both in terms of acidic strengths and the number of acid sites, of zeolitic substances.

Acknowledgement

The authors gratefully acknowledge financial assistance for the project from Taiwan National Science Council, National Science Foundation (#9402636) and a Research Initiation Grant of the University of Louisville

References

[1] J.W. Ward and R.C. Hansford, J. Catal. 13 (1969) 364.
[2] A.I. Biaglow, D.J. Parrillo and R.J. Gorte, J. Catal. 144 (1993) 193.
[3] J. Datka, B. Gil and A. Kubacka, Zeolites 15 (1995) 501.
[4] A.G. Pelmenschikov, J.H.M.C. van Wolput, J. Janchen and R.A. van Santen, J. Phys. Chem. (1995) 3612.
[5] L. Smith, A.K. Cheetham, R.E. Morris, L. Marchese, J.M. Thomas, P.A. Wright and J. Chen, Science 271 (1996) 799.
[6] A. Corma, A.L. Agudo and V. Fornes, J. Chem. Soc. Chem. Commun. (1983) 942.
[7] J. Datka, J. Chem. Soc. Faraday Trans. I 77 (1981) 2877.
[8] D. Freude, M. Hunger, H. Pfeifer and W. Schweiger, Chem. Phys. Lett. 128 (1986) 62.
[9] H. Pfeifer, D. Freude and M. Hunger, Zeolites 5 (1985) 275.
[10] T. Gross, U. Lohse, G. Engelhart, K.H. Richter and V. Patzelova, Zeolites 4 (1984) 25.
[11] Z. Gog, Y. Tog and Z. Yugin, Appl. Catal. 56 (1989) 83.
[12] A.T. Shakhtakhtinskaya, Z.M. Mamedova, S.F. Matallibova, S.Z. Alieva and R.G. Mardzhanova, React. Kinet. Catal. Lett. 39 (1989) 137.
[13] *The 11th International Conference on Positron Annihilation*, Kansas City, 1997.
[14] W.F. Huang and D.C. Huang, Appl. Phys. Lett. 63 (1993) 1334.
[15] W.F. Huang, D.C. Huang and P.K. Tseng, Catal. Lett. 26 (1994) 269.
[16] W.F. Huang, D.C. Huang, K.J. Hung and P.K. Tseng, Catal. Lett. 40 (1996) 31.
[17] K.J. Hung, Ph.D. dissertation, University of Louisville (1997).
[18] C.C. Huang, Ph.D. dissertation, National Taiwan University (1997).
[19] Z. Gao, Y. Tang and Y.G. Zhu, Appl. Catal. 56 (1989) 83.
[20] R.A. van Santen, Stud. Surf. Sci. Catal. 85 (1994) 273.