Surface acidity by positron annihilation lineshapes

W.F. Huang

Department of Physics, University of Louisville, Louisville, KY 40292, USA

D.C. Huang

Research and Development, United Catalysts, Inc., Louisville, KY 40210, USA

and

P.K. Tseng

Department of Physics, National Taiwan University, Taipei, Taiwan ROC

Received 28 January 1994; accepted 18 March 1994

An alternative new method to measure the specific acidity of catalytic materials with large internal surface areas by using positron annihilation spectroscopy was introduced. Results of lineshape parameter evaluations from two-dimensional angular correlation and Doppler broadened annihilation radiation measurements for a zeolite ZSM-5 were presented.

Keywords: acidity; catalysts; positron annihilation spectroscopy; zeolite ZSM-5

1. Introduction

Industrial chemical processes often use catalytic materials which have large internal surfaces to promote reaction rates. Zeolite catalysts in particular play vital roles in many sectors of the chemical industry. ZSM-5, for example, is invaluable in many large scale processes such as M-forming (increasing octane number in gasoline), dewaxing, high yield ethylbenzene production and methanol conversion to high grade gasoline, etc. [1].

The catalytic process is rather complicated. It involves many factors such as diffusion and adsorption of reactants on the catalyst surface, and also desorption and diffusion of products away from the surface. It is therefore conceivable that the physical and chemical characteristics of the internal surface can critically affect the activity and performance of a zeolite catalyst [2].

In the nowadays increasing public demand for improved air quality as enforced by government regulations and industrial pressure to achieve better fuel efficiency, the need to understand and to search for improved newer ways of characterizing the internal surface of zeolitic materials has become ever more important and urgent.

Conventional experimental methods for surface acidity evaluation include UV-visible spectroscopy (Hammett-type measurements), study of thermal deposition of salts, measurements of heat of interaction with bases, and measurements of rates of model reactions, etc. While all these methods have been employed traditionally, each one of them imposes certain limitations on its applicability. The Hammett-type measurements are not usable for most practical purposes, because actual catalysts for industrial applications are normally colored and opaque. The thermogravimetric and calorimetric techniques have not been able to distinguish the effects of protonation of the base from the effects of other types of interaction of the base with the catalyst. The method based on reaction kinetics requires a thorough knowledge of the reaction mechanism itself, which is often based upon postulations. The chemisorption method for determining the surface area and acidity of zeolites depends on the type and properties of the molecules used. It often yields inconsistent results and fails to provide a valid assessment on the activity of the zeolite. The application of the C-13 NMR method for the measurement of protonation has a low sensitivity and requires the use of concentration of base whose cancellation of the activity term is not usually known [3].

In this report we present evidence, for the first time, of the direct correlation between positron annihilation radiation lineshapes and surface acidity for the zeolite catalysts ZSM-5. The results greatly enhance the potential of applying positron annihilation spectroscopy (PAS) for surface studies.

2. Experimental

PAS has been acknowledged as an in situ microprobe for monitoring electronic and defect properties of a great variety of materials [4]. Its application for studies of catalytic materials has been, however, rather modest [5]. The method consists of three techniques, i.e., positron annihilation lifetime (PAL), one- and two-dimensional angular correlation of the annihilation radiation (1D- and 2D-ACAR), and Doppler broadened annihilation radiation (DBAR) measurements [6].

PAL spectroscopy, which was almost exclusively employed for the characterization of catalytic and porous materials by other researchers in their earlier investigations, often has complex multi-component structures for molecular substances [7–11]. Its data acquisition is usually time consuming, and its analysis trying. We report here results of 2D-ACAR and DBAR measurements and demonstrate their utilities and effectiveness for surface characterization studies.

The annihilation gamma ray from solids has a wide Doppler broadened energy distribution curve centered at 511 keV, which is measured by a high resolution Ge detector system, and the angular correlation curve of the two emerging annihilation gamma rays relates to the momentum distribution of the positron–electron pairs in the sample. Some of the positrons impregnated in the target sample will form positronium atoms (Ps). Gamma rays from the eventual collapse of positronium atoms

have a much narrower energy and momentum distributions superimposing over the regular wide Gaussian-shaped energy and momentum distribution curves and thus contribute to the intensity of the central region of the total gamma ray spectrum. Consequently, any change in the positronium population in the sample will induce a corresponding change in the over-all shape of the energy and momentum curves that are monitored by using a lineshape parameter S, which is defined as the ratio of the area of the narrow central region of the distribution curve and the total area under the curve.

In porous materials such as zeolite catalysts, positrons emerging from the bulk experience a negative work function at the surface and form positroniums only on the near surfaces with a certain likelihood, not in the crystalline bulk [12]. The population of the positronium atoms on the surface and hence the shape of the energy or momentum distribution curve of the annihilation gammas is affected by surface characteristics such as surface area and surface acidity. Positronium is known to interact preferentially with Brønsted acid sites [8], and its population has been demonstrated to increase with the surface area [9].

As a common practice, radioisotope Na-22 with an activity of about 10 mCi was used as the positron source in this experiment. The positrons with a continuous energy distribution typical of a beta decay process penetrate different depths in the specimen, and thus sample a variety of internal surfaces. Annihilation spectra from 2D-ACAR measurements and from supplemental DBAR measurements (for the purpose of comparison) were collected and displayed on multi-channel analyzers through conventional gamma spectrometer systems.

3. Results and discussion

Fig. 1 exhibits a typical 2D-ACAR spectrum of a ZSM-5 sample in ammonium form. The central sharp peak evidenced the contribution from annihilations of positronium atoms. A slice cut through the center of the 2D spectrum was used for the evaluation of the lineshape parameter S which, throughout the experiment, is defined as the ratio of the area within the central $+/-$ 7 channels and the area within $+/-$ 100 channels for the 2D-ACAR spectrum, and $+/-$ 10 channels and $+/-$ 100 channels for the DBAR spectrum, which employs a simpler instrumentation but has a lesser resolution than the 2D-ACAR technique. Fig. 2 shows a thermogravimetric analysis (TGA) of the NH_4-ZSM-5. The rapid drop in the region 250–500°C has been identified to be due to the loss of NH_3 as a result of thermal decomposition,

$$NH_4^+\text{-ZSM-5} \rightarrow H^+\text{-ZSM-5} + NH_3 .$$

The surfaces Brønsted acidity of the sample therefore increases as more NH_3 is released in this temperature region. The protonic acidity reduces positronium

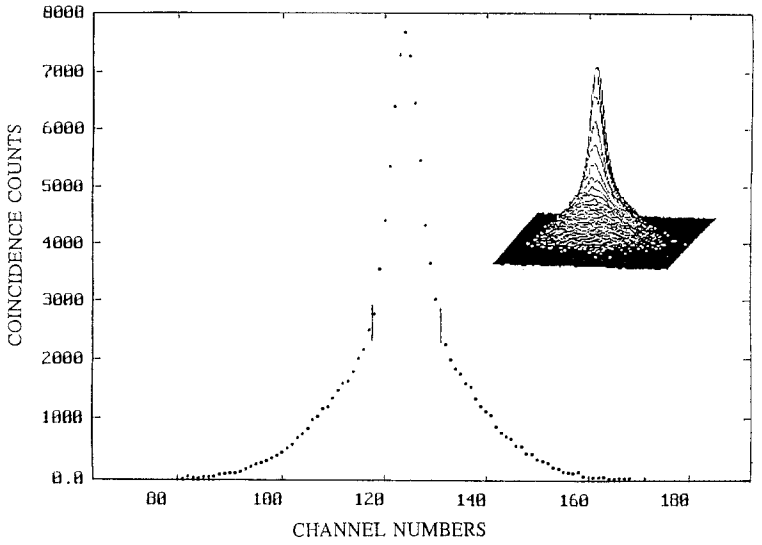

Fig. 1. A typical 2D-ACAR spectrum of a NH_4^+-ZSM-5 sample and a cross sectional view through the center of the spectrum. A small vertical bar indicates the range of data points used for evaluating the lineshape parameter S.

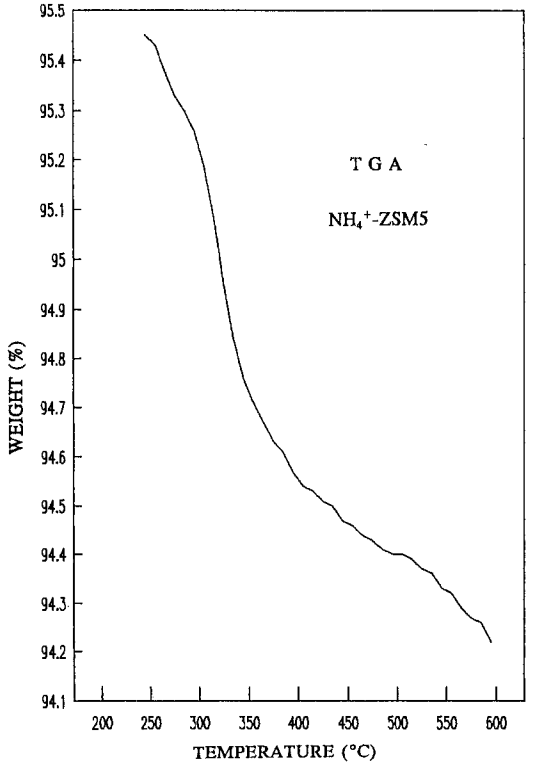

Fig. 2. A TGA versus temperature plot for the NH_4^+-ZSM-5 sample.

population through oxidation of Ps atoms by protons [13] and thus diminishes the value of the lineshape parameter S. Fig. 3 exhibits a plot of lineshape parameter S from 2D-ACAR measurements. Several data points from DBAR measurements were also shown in the figure for the purpose of comparison and to illustrate the consistency between the two methods. It clearly shows that there is a corresponding rapid decrease of S values in the temperature region where the TGA values diminish. The correlation between surface acidity and parameter S is thus strongly demonstrated.

Results of previous experiments have shown that the lineshape parameter S increases with the surface area of the material [14]. Therefore, the S value is expected to decrease as the specific acidity (protonic acidity per unit surface area) of the sample increases. The surface areas of several NH_4^+-ZSM-5 samples which have been calcined at temperatures where TGA results indicate significant weight losses have been determined by nitrogen absorption at liquid nitrogen temperature. The results are contained in table 1.

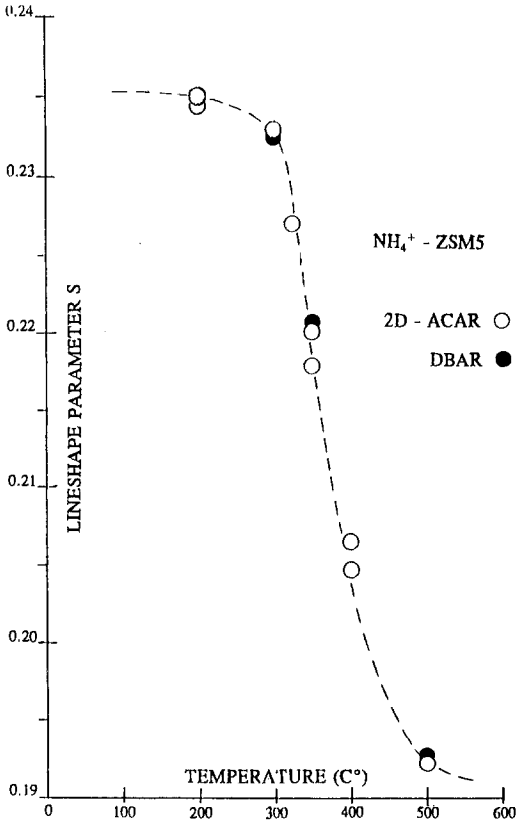

Fig. 3. A plot of lineshape parameters S from 2D-ACAR (open circles) and DBAR (solid circles, scale not shown for clarity) versus temperature.

Table 1

Temperature (°C)	Surface area (m^2/g)
250	458
300	453
325	432
340	444
375	420
500	430

The acidities of these samples which have been calcined in the 250–500°C region were evaluated from the TGA measurements in terms of relative weight loss at these temperatures with respect to that at 250°C. Fig. 4 presents the plot of the lineshape parameter S versus the relative specific acidity (relative surface proton concentration denoted by H). It clearly demonstrates a linear correlation between the H and S values.

In conclusion, we have presented ab initio results from 2D-ACAR and DBAR measurements of a NH_4^+-ZSM-5 zeolite catalyst, and amply demonstrated the utility and effectiveness of using the simple lineshape parameter S to monitor the specific acidity of the zeolite. The findings presented here point out the fact that such lineshape measurements of PAS can well be an effective in situ microprobe that could have important practical applications in internal surface characterization of zeolitic catalysts in general. It has demonstrated that the method is capable of making crucial contribution to the understanding of the mechanism of catalytic activity and performance.

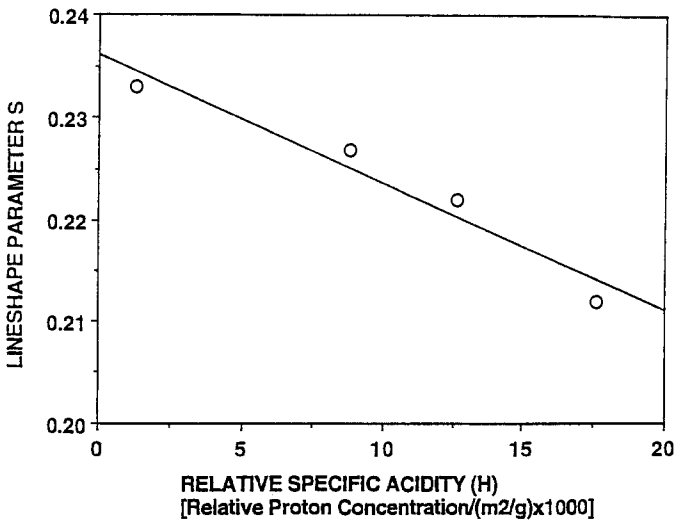

Fig. 4. A plot of S parameter versus relative specific acidity (H) for the NH_4^+-ZSM-5 sample.

Acknowledgement

The authors wish to express their gratitude to J. Ladebeck of Sued Chemie A.G. for his useful advices, L. Hulett for his helpful discussions, R. McCoy for her TGA evaluations, and C.C. Huang, J.T. Lin, Y.C. Pan and S.Y. Lin for their gracious assistance in conducting the 2D-ACAR measurements. This work was supported in part by research initiative grants of the University of Louisville.

References

[1] A. Dyer, *An Introduction to Zeolite Molecular Sieves* (Wiley, New York, 1988).
[2] S. Bhatia, *Zeolite Catalysis: Principles and Applications* (CRC Press, Boca Raton, 1990).
[3] D. Farcasiu, G. Miller, A. Ghenciu and H.S. Cao, 13th North American Meeting of the Catalysis Society, Pittsburgh, 2–6 May 1993.
[4] *Proc. 9th Int. Conf. on Positron Annihilation*, Parts I–III, Szombathely 1991; *Proc. 4th Int. Workshop on Positron and Positronium Chemistry*, Le Mont Sainte-Odile 1993.
[5] J. Lahtinen and A. Vehanen, Catal. Lett. 8 (1991) 67.
[6] D.M. Schrader and Y.C. Jean, *Positron and Positronium Chemistry* (Elsevier, Amsterdam, 1988).
[7] K. Venkateswaran, K.L. Cheng and Y.C. Jean, J. Phys. Chem. 88 (1984) 2465.
[8] Y. Ito and T. Takano, Appl. Phys. A 45 (1988) 193.
[9] M.B. Perkal and W.B. Walters, J. Chem. Phys. 53 (1970) 190.
[10] H. Nakanishi and Y. Ujihira, J. Phys. Chem. 86 (1982) 4446.
[11] Z. Gao, X. Yang, J. Cui and Y. Wang, Zeolites 11 (1991) 607.
[12] P.M. Platzman and N. Tzoar, Phys. Rev. B 33 (1986) 5900.
[13] W.F. Huang, R. Ochoa and R. Miranda, Phys. Lett. A 158 (1992) 417.
[14] W.F. Huang and D.C. Huang, Appl. Phys. Lett. 63 (1993) 1334.