PERGAMON

Radiation Physics and Chemistry 58 (2000) 715–718

Radiation Physics and Chemistry

www.elsevier.com/locate/radphyschem

Positronium formation in NaY-zeolites studied by lifetime, positron beam Doppler broadening and 3-gamma detection techniques

H. Schut[a,*], Galindo R. Escobar[a], Z.I. Kolar[a], A. van Veen[a], G. Clet[b]

[a]*Interfaculty Reactor Institute, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands*
[b]*Laboratory of Organic Chemistry and Catalysis, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands*

Abstract

Results of positron annihilation measurements on NaY pressed powders and deposited thin films using slow positron beam and conventional fast positron techniques are presented. In lifetime experiments using an external ^{22}Na source an averaged long lifetime of 1.8 ns with a sum intensity of 27% was observed in pressed powders in the presence of air at room temperature (RT). In literature this lifetime is ascribed to positrons annihilating in water filled α or β cages Habrowska, A.M., Popiel, E.S., 1987. Positron annihilation in zeolite 13X. J. Appl. Phys. 62, 2419. By means of isotopic exchange some of the Na was replaced by ^{22}Na. These powders showed a long lifetime component of 7–8 ns with an intensity increasing from 1 to 12% when heated under normal atmosphere from RT to 200°C. No significant increase of the shorter (1.5 ns) lifetime was observed, while its intensity dropped from 13.4 to 6.6%. Both effects are ascribed to the loss of water from α cages only. The beam experiments revealed a high fraction of 3-gamma annihilations in the pressed powder and thin film samples, indicating the annihilation of o-Ps and thereby the existence of large open volumes.

Keywords: Positron; Positronium; Zeolites

1. Introduction

The application of the positron lifetime and Angular Correlation of Annihilation Radiation (ACAR) techniques in conjunction with the study of voids such as so called α and β cages in different types of zeolites is discussed by Ito et al. (1988). Others have used positrons to study dehydration, annealing (Habrowska and Popiel, 1987), impregnation (Debowska et al., 1986) of zeolites as well as the shape of voids in zeolites (Hasegawa et al., 1992). All these studies involved (pressed) zeolite powders in combination with an encapsulated or deposited, external ^{22}Na source emitting fast positrons.

In this paper we present results obtained with NaY pressed pellets and thin deposited layers using the Variable Energy Positron beam (VEP) facility at Delft. In addition, as a pilot for future 'in situ' studies of zeolites, positron lifetime measurements on NaY powders in which sodium has been replaced by ^{22}Na have been carried out.

* Corresponding author. Tel.: +31-15-278-1961; fax: +31-15-278-6422.
E-mail address: Hschut@iri.tudelft.nl (H. Schut).

0969-806X/00/$ - see front matter
PII: S0969-806X(00)00245-0

2. Materials

Pellets of NaY were produced by pressing binder free zeolite powder containing 13.38 wt% of Na_2O (CBV100 from Zeolyst) into disks of 10 mm in diameter and of approximately 1 mm thickness at a pressure of 300 N/cm^2. Prior to pressing, the powder was dried at 110°C for 15 h. The amount of water released (20% of the total weight) was determined by weighing the sample before and immediately after the drying process. Keeping the pellets under normal atmospheric conditions (as is the case during recording of lifetime spectra) results into a complete uptake of water (saturation) from air within 1–2 h.

Zeolite NaY thin layer samples were grown on a stainless steel substrate using a so called "seeded syntheses mixture" (Clet et al., 1999). For better adhesion of the layer the substrate surface has been thermally oxidized in air prior to growth. Scanning Electron Microscope (SEM) images showed a zeolite layer thickness of typically 1.5 μm. After preparation the samples were kept under atmospherical conditions.

Samples with built in ^{22}Na radioisotope (Amersham) were produced by means of isotopic exchange. NaY powder was dispersed in an aqueous NaCl solution containing 10% of the sodium present in the zeolite and 54 μCi (2.0 MBq) of $^{22}Na^+$. After reaching the (isotopic) exchange equilibrium the powder was separated from the suspension by centrifugation and washed with distilled water several times to be sure that the positron emitter is only in the pores of the zeolite. This was monitored by measuring the activity of the supernatants. After separation and drying, 1 g of NaY powder with an activity of about 50 μCi (92.5% of the initial activity)[1] was obtained. The powder was put into a thin walled aluminium container. A resistive heater wrapped around the container allowed for heating the powder in air during recording of lifetime spectra.

3. Experimental

Positron lifetime spectra were recorded using a fast–fast coincidence set up with internal dynode read out (deVries, 1987). The time resolution of this system was 175 ps (FWHM, ^{60}Co). In case of the NaY pellets a 200 μCi ^{22}Na source was encapsulated between two 7 μm thick kapton foils. The source contribution to the spectra was about 25%. The time required to accumulate a spectrum containing (1–7) × 10^6 events was typically 2–15 h. Lifetime spectra were analysed assuming four lifetime components using the POSITRONFIT program (Kirkegaard et al., 1981). No source contribution was accounted for in the case of the samples with an internal ^{22}Na source. The lifetime resolution function was assumed to be identical for both types of samples.

The beam experiments were carried out with the Delft Variable Energy Positron beam facility (VEP) (Schut, 1990). A pressed pellet and a deposited thin layer of NaY on a stainless steel substrate were injected with positrons (10^5 s^{-1}) with energies tuned between 100 eV and 25 keV. Annihilation spectra were recorded with single Ge solid-state detector as a function of the positron implantation energy. Analysis was made of the Doppler broadening (S) of the 511 keV photo-peak (2-γ events) and the annihilation of o-Ps contributing to the total spectrum (3-γ events). This contribution is quantified by a parameter $R = T/P$-1 where T is the number of counts in the gamma energy region from near 0 to 511 keV and P is the number of counts in the 511 keV line. By proper scaling, the value of R can be related to the fraction of Ps formed in (or at the surface) of the sample (Schut, 1990; Mills, 1983). All beam experiments were carried out under vacuum conditions of about 10^{-6} Pa. In addition, the deposited layer sample has been subject to an in situ

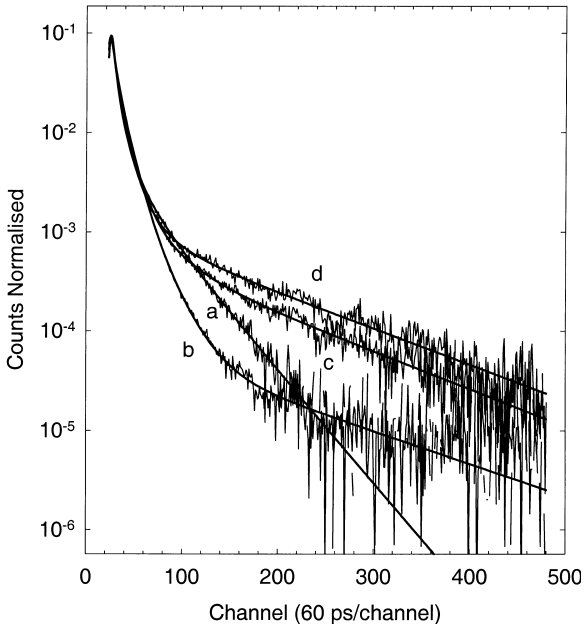

Fig. 1. NaY Positron lifetime spectra and fitted curves (POSITRONFIT) for: (a) pressed pellet at RT, (b) NaY powder with internal source at RT, (c) as (b) at 110°C and (d) as (b) at 200°C. Data are normalised by the total number of counts.

[1] This was an expected value. 1 g of CBV100 zeolite contains 50 mg of Na and the solution 5 mg, so the proportion of Na in the zeolite should be 0.909 (50/55) and 0.091 (5/55) in the solution after exchange.

annealing at 600°C for 30 min. After cooling down to RT and measuring S and R the sample has been exposed to air for 1.5 h. After evacuation the S and R measurements have been repeated once more.

4. Results

4.1. Lifetime experiments

Fig. 1 shows the measured positron lifetime spectra and fitted curves in the case of: (a) a pressed NaY pellet in air at RT with an external ^{22}Na source; (b) NaY powder with internal ^{22}Na source at RT in air; (c) as (b) but at 110°C and (d) as (b) but at 200°C. The fitted values of the lifetime components τ_3 and τ_4 and their intensities I_3 and I_4 are summarized in Table 1. For the sample with external source the average of τ_3 and τ_4 (weighed by their intensities) gives a lifetime of 1.8 ns. This value is mentioned in literature (Habrowska and Popiel, 1987) and is ascribed to fully hydrated zeolites. The values for the other two lifetimes are 0.17 and 0.6 ns and are attributed to p-Ps and free-positron annihilation, respectively.

4.2. Beam experiments

The results of the positron beam experiments on a NaY pressed pellet and a thin deposited layer are shown in Fig. 2. The position of the interface between NaY and substrate is seen by the plateau in the Doppler data in curves b, c and d at 7–8 keV. With a simple relation correlating the mean positron implantation depth to a density of 2 g/cm^3 (derived from the stoichiometry) and implantation energy one estimates a layer thickness of about 0.5 μm. The fact that from SEM images a layer thickness of approximately 1.5 μm is derived indicates that the actual density of the layer is 1/3 of the assumed density. This is indeed measured for the bulk density of the powder pellets. For the estimation of the positronium fraction system specific scaling parameters need to be known. These parameters depend on, for instance, the detector-sample geometry, materials surrounding the sample and basically define annihilation spectrum recorded in case of 0 and 100% Ps formation. For the data presented here, parameters are taken from e^+ and Ps emission measurements on tungsten moderator foils and therefore some uncertainty in the exact absolute values may be introduced.

5. Discussion and conclusions

5.1. Lifetime

In the zeolite with internal ^{22}Na source a long lifetime component of 7.8 ns with an intensity of 1% was observed at RT. With an external source such a component was not detected under the same experimental conditions (room temperature and total number of counts) We attribute this effect to the difference between the amount of source contribution for the two types of samples. In case of an external source this contribution amounts to 25% and stems from the kapton foil and the sodium salt. For the internal source the contribution of the aluminium container was calculated to be less than 1% based on the implantation profile for fast positrons and geometry of the container. Another reason for the presence of the long lifetime in the sample with internal source may be the presence of open spaces in the unpressed powder. This will be further investigated by performing measurements on pressed samples with internal source. At 200°C an increase of the intensity of the long lifetime component in the sample with internal source is observed. In studies done by (Habrowska and Popiel, 1987) this increase for samples with external source has been attributed to the release of water from the α cages. If the remaining I_3 contribution is associated to the smaller β cages then from the corresponding lifetime τ_3 it can be concluded that under the condition applied water is still present in these cages.

5.2. Beam experiments

For the as-prepared samples a high yield of 3-γ events is observed. By proper scaling and assuming a ortho- to para-Ps formation ratio of 3:1 an o-Ps frac-

Table 1
Fitted values for lifetime components τ_3 and τ_4 and their intensities I_3 and I_4 measured in NaY pellets and powder with external and internal source

Source/temp	Curve in Fig. 1	τ_3 (ns)	τ_4 (ns)	I_3 (%)	I_4 (%)
External/RT	a	1.122 ± 0.260	2.269 ± 0.140	11.7 ± 1.8	15.1 ± 3.4
Internal/RT	b	1.214 ± 0.042	7.854 ± 0.481	13.4 ± 1.3	1.0 ± 0.05
Internal/110°C	c	1.832 ± 0.095	7.294 ± 0.143	7.6 ± 0.4	7.3 ± 0.2
Internal/200°C	d	1.513 ± 0.289	7.117 ± 0.194	6.6 ± 1.8	12.1 ± 0.4

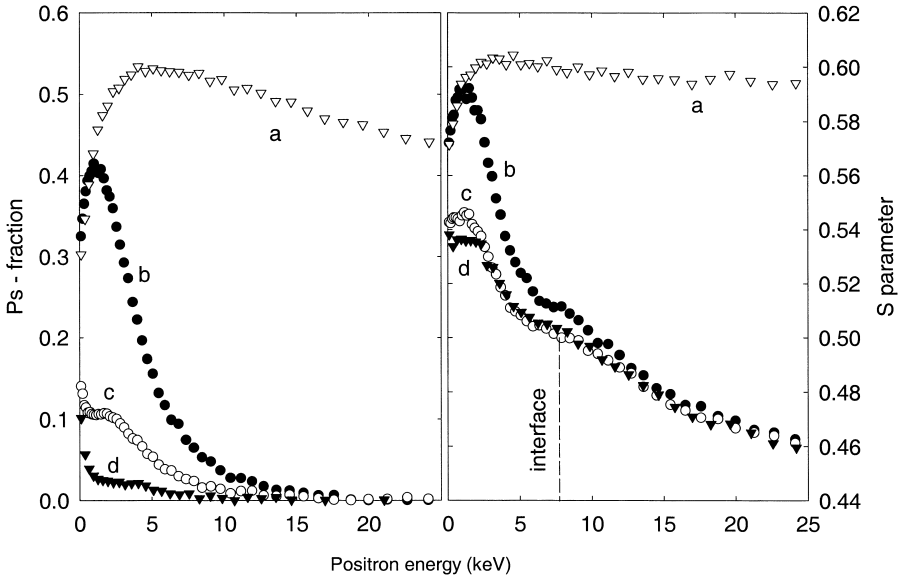

Fig. 2. Positronium fraction (left) and Doppler *S*-parameter (right) as a function of the positron implantation energy. (a) NaY pressed pellet (same as curve a in Fig. 1) , (b) deposited NaY layer on substrate, (c) layer after annealing in vacuum at 600°C (d) as (c) followed by exposure to air for 1.5 h. All measurements are done at RT and 10^{-6} Pa vacuum.

tion of about 37% (in the pressed pellet) is obtained. Due to the limited thickness this value is not reached in the layer sample. On the other hand, the similar behaviour of both the Ps- and Doppler-data at low energies indicate that such a high fraction is likely to be present in the thin layer. Annealing at 600°C (heating rate 50°C/min) results in a drop in both Ps fraction and *S* parameter. Exposure to air and re-evacuation did not restore the previous data but showed further decrease. The drop in Ps-fraction and *S* parameter after heating is likely due to the high heating rate causing a collapse of the zeolite framework and thus reducing the fraction of open-volume.

References

Clet, G., Jansen, J.C., Bekkum van, H., 1999. Synthesis of a zeolite Y coating on stainless steel support. Chem. Mater. 11 (7) in press.

Debowska, M., Baranowski, A., Jerie, K., Swiatkowski, W., 1986. The effect of impregnation with gold on positron lifetime spectra in NaY zeolite. Phys. Stat. Sol (a) 97, 35.

Habrowska, A.M., Popiel, E.S., 1987. Positron annihilation in zeolite 13X. J. Appl. Phys. 62, 2419.

Hasegawa, M., Tsuchiya, Y., Kitayama, Y., Ciba, T., Saitoh, M., Yamaguchi, S., 1992. Positronium in zeolitic materials — sepiolite-. Mater. Sci. Forum 105 (110), 257.

Ito, Y., Takano, T., Hasegawa, M., 1988. Positron annihilation in synthetic zeolites. Appl. Phys. A 45, 193.

Kirkegaard, P., Eldrup, M., Mogensen, O., Pedersen, N.J., 1981. Program system for analysing positron lifetime spectra and angular correlation curves. Comp. Phys. Commun. 23, 307.

Mills Jr, A.P., 1983. Experimentation with low energy positron beams. In: Positron Solid-State Physics. North Holland, Amsterdam, p. 432.

Schut, H., 1990. A variable energy positron beam facility with applications in materials science. Thesis, Delft University of Technology, Delft, The Netherlands.

deVries, J., 1987. Positron lifetime technique with applications in materials science. Thesis, Delftse Universitaire Pers, Delft, The Netherlands.