POSITRON ANNIHILATION LIFETIME SPECTROSCOPY APPLICATION IN STRUCTURAL INVESTIGATIONS OF LOW-SILICA ZEOLITES AND THEIR AMORPHOUS PRECURSORS

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ABSTRACT

In this work a short review of recently obtained results is shown. Positron annihilation lifetime spectroscopy has been efficiently used for investigations of the zeolite precursors structure influenced by presence of different alkali cations. Also, stages of zeolite A crystallization and the effect of dehydration of low-silica zeolites on the free volume of structural cages in correlation to the number and atomic sizes of non-framework cations present have been monitored.

Keywords: positron annihilation, zeolite, precursor.

INTRODUCTION

Positron annihilation lifetime spectroscopy (PALS) is sensitive and proved method for material structure investigations. Positrons are sensitive probes for vacancies, voids and inner surfaces of different materials and are valuable tool for investigation of average pore size, pore size distribution and connectivity as well as surface properties of different materials [1]. Characterisations of micropore structures enable understanding the influence that configuration of void network as well as morphology of pores have on the mechanical, thermal and permeability properties and behaviour of materials.

We have used PALS for structural investigations of differently treated and prepared amorphous precursors [2]. Detected voids could be connected to the structural entities and nuclei formed during precipitation, and their sizes and distribution can be significantly influenced by the type of alkali cation present and also by temperature and time duration of precursor ageing.

Dehydration of zeolites A, X and Y during drying at predetermined temperatures was also monitored by PALS and obtained results have been compared and discussed from the point of their different Si/Al ratio and sizes of alpha and beta cages [3].

In PALS investigation of stages of zeolite A crystallization, structural changes, specifically, void sizes and their concentration, have been monitored [4]. Samples for PALS measurements were taken at the early beginning of the crystallisation process (gel), during the process, and at the end of the process (zeolite).

EXPERIMENTAL

Syntheses and preparations of the samples for the investigation of different alkali cation influence, drying of low-silica zeolites experiments, and zeolite A crystallization monitoring are explained in references [2], [3] and [4], respectively. In general, silicate and aluminate component of defined concentration were prepared then mixed. Precipitated amorphous precursors (gels) where then used as prepared for hydrothermal treatment or modified. All the final samples (zeolites and precursors) were centrifuged to separate liquid from solid phase, and the solid phase was then successively washed and centrifuged several times. The washed samples were dried overnight in a drying chamber. For the PALS measurements, dried and powered zeolite and zeolite precursor samples were pressed into pellets of 13 mm diameter and about 2 mm thickness.

RESULTS AND DISCUSSION

In such complex systems, as zeolites and zeolite precursor gels, various lifetime components can appear reflecting material structure. Up to four lifetime components, $\tau_1 - \tau_4$, were used in the fitting procedure for resolving our experimentally obtained lifetime spectra. For example, experimental and theoretical curves obtained for sample Cs gel prepared by procedure b are shown in Figure 1.
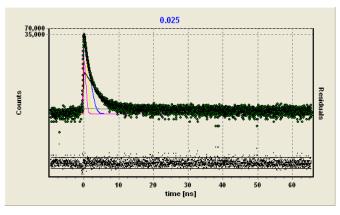

Figure 1. Experimental (○) and theoretical (—) curves obtained for analyzed spectrum of Cs gel prepared by procedure b.

The first (τ_1) and second (τ_2) lifetime components are connected to annihilation of *para*-positronium, free positrons and trapped positrons. The third and fourth lifetime components represent long-lived *ortho*-positronium states, probably trapped at various free volume sites. The existence of the long *ortho*-positronium lifetimes (τ_3 and τ_4) in the investigated samples, in fact, indicates the presence of void features, different micro-, meso- and macropore structures, and only these will be discussed further. Their intensity values (I_3 and I_4) can be connected to the concentration of those sites. Trapped *ortho*-positronium interacts with the electrons of the void inner surface, and finally it annihilates with one of them into two gamma rays by so called "pick-off process". In the simple quantum mechanical model of spherical holes, developed by Tao and Eldrup [5,6], these pick-off lifetimes, up to approx. 10 ns, can be connected with the hole (void) size by the relation:

$$\frac{1}{\tau} = \lambda_b \left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin\left(2\pi \frac{R}{R + \Delta R} \right) \right]$$

(1)

where τ is positronium lifetime in ns, R hole radius in nm, ΔR=0.156 nm, and λ_b=2 ns^{-1}.

Influence of alkali cation

The third lifetime components, τ_3, measured on the gels prepared directly from MeOH (Me= Na$^+$, K$^+$, Rb$^+$, Cs$^+$) by the procedure a [2], are in the range of 0.94 – 1.30 ns (Table 1). The sizes of the voids obtained from lifetimes decrease in order Cs$^+$, Rb$^+$, Na$^+$ and K$^+$. These differences are ascribed to the different influence of the cation on the surrounding reactive species that changes the nature of alkali cation – aluminosilicate anion complexes. On the other hand, in the case that the cations are introduced in the matrix by ion exchange, (procedure b, [2]) the τ_3 lifetimes are approximately the same for all the cations (Table 2) and the size of cation does not have such pronounced influence. The higher intensities I_3 measured for ion exchanged gels, compared to I_3 of gels prepared by procedure a, are probably the result of the different silica source. The fourth lifetime components, τ_4, have values in the

range of 2.7 - 5.0 ns (Table 1 and 2). These lifetimes have also lower intensities than τ_3, suggesting the presence of the larger voids already in the initial phase of zeolite formation, but in a smaller extent. In this case the correlation to the influence of cation sizes cannot be established.

Table1. Lifetimes τ and intensities I measured on the gels prepared by procedure a.

Sample	τ_3(ns)	I_3(%)	τ_4(ns)	I_4(%)
Na gel	1.01±0.04	9.6±0.3	3.9±0.5	1.1±0.1
K gel	0.94±0.07	9.0±0.8	3.2±0.4	1.4±0.3
Rb gel	1.15±0.13	5.4±0.5	2.9 ±0.3	1.8±0.4
Cs gel	1.30±0.07	7.3±0.3	5.0±0.4	2.3±0.2

Table 2. Lifetimes τ and intensities I measured on the gels prepared by procedure b

Sample	τ_3(ns)	I_3(%)	τ_4 (ns)	I_4 (%)
Na gel	0.91±0.03	12.6±0.6	3.7±0.2	1.06±0.08
K gel	0.89±0.03	11.5±0.8	3.8±0.3	1.6±0.1
Rb gel	0.96±0.01	11.65±0.08	3.96±0.15	1.21±0.03
Cs gel	0.94±0.09	11±1	2.7±0.4	1.8±0.5

Zeolite A crystallisation

The lifetime spectra obtained by PALS investigations of zeolite A crystallisation contain four components. Calculated sizes of free volumes from long lifetimes τ_3 and τ_4 using Tao-Eldrup model, equation (1), and sum of their intensity values I_3 and I_4 are shown in Figure 2. The sizes of free volumes are rather constant. Intensity values, I_3 and I_4, initially decrease during induction period, and then increase with the crystallisation time. Heating of the reaction mixture to the reaction temperature during induction period is causing reorganisation of structural entities that have been formed during precursor precipitation and that is reflected in the change of intensity values.
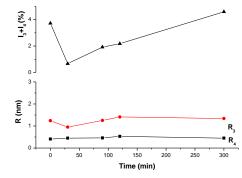

Figure 2. Free volume sizes R and sum of intensities I_3+I_4 as a function of time duration of the crystallisation process.

The sizes of free volumes are in range of sizes of zeolite A channels and cavities and their concentration is increasing, as the increase of the sums of their relative intensity values shows. That indicates that during zeolite synthesis more characteristic structural entities are appearing, building specific zeolite structure.

Water removal from zeolite structure

The third τ_3 and fourth τ_4 lifetime components from PALS results obtained during drying of zeolites A and Y at 80, 100,140 and 180 °C are shown in Table 3. In non dried RT samples, long component shows that even in such "crowded" environment o-Ps is present in relatively large quantities, formed probably on the framework surface, with, for example, lifetime in Y comparable to the o-Ps lifetime found in bulk water (1,8 ns).

Long lifetimes obtained in zeolite samples dried at 80, 100 140 and 180 °C, are splitting into two components (τ_3 and τ_4), showing change in distribution of free voids in samples as a

consequence of water molecules removal from the inside of the structure. Lifetime intensities (I_3+I_4) vary in small range (A) or are rather constant (Y).

Table 3. Lifetimes τ and intensities I obtained during drying of zeolites.

	ZEOLITE A				ZEOLITE Y			
	τ_3(ns)	I_3(%)	τ_4 (ns)	I_4 (%)	τ_3(ns)	I_3(%)	τ_4(ns)	I_4 (%)
RT	1.433±0.006	14.0±0.1	-	-	1.869±0.008	14.5±0.1	-	-
80 °C	2.54±0.03	12.7±0.1	6.34±0.04	4.8±0.1	2.26±0.05	9.9±0.1	12.5±0.9	1.99±0.06
100 °C	2.64±0.06	10.9±0.2	7.3 ±0.4	2.9±0.3	2.13±0.03	9.1±0.2	27.7 ±0.6	2.56±0.03
140 °C	1.4±0.2	5.2±0.5	4.30±0.07	9.8±0.4	1.91±0.03	8.4±0.2	32.1±3.9	3.2±0.4
180 °C	1.7±0.2	5.9±0.4	4.5±0.3	7.6±0.4	1.97±0.03	8.2±0.1	33.3±2	3.5±0.3

Although the same temperature regime has been applied for all three zeolites, differences of positron and positronium lifetime values obtained have been found. They could be ascribed to different structures of zeolites (LTA for zeolite A and FAU for X and Y zeolites), but also to the different Si/Al ratio in zeolites from the same structural groups (zeolites X and Y). Their intensity values are rather constant for all drying temperatures and lifetime values, corresponding to the voids in which they annihilate, increase with drying temperature for all zeolite samples, except in zeolites A and Y dried at 140°C. Water removal from zeolite structure empties space, but also framework oxygen atoms become more exposed and their pronounced interaction with positronium can probably explain decrease of lifetimes in zeolites A and Y.

CONCLUSIONS

Some of our results of structural investigation of zeolites and their precursors obtained by PALS have been reviewed. They indicate different influence of Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ cations on the structure of zeolite precursor gel. Also, it was found that removing of water molecules from zeolite structure, depending on the zeolite structure type and Si/Al ratio, significantly influence positron lifetimes and its intensity values. During crystallisation of zeolite A, sizes of free volumes are rather constant, but their concentration is increasing connected to the more ordered structure emerging during the process.

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