

POSITRON ANNIHILATION LIFETIME SPECTROSCOPY (PALS) IN STRUCTURAL INVESTIGATIONS OF ZEOLITES – AN OVERVIEW OF THE EXPERIMENTAL RESULTS

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ABSTRACT

PALS is well established method for structural investigation of different materials that contain voids or imperfections of nanoscale dimensions, such as metals and alloys, semiconductors and different porous materials as well as zeolites. In this work, several examples of its use in structural investigation of zeolites, zeolite precursors and related materials have been shown and discussed.

Keywords: positron, structure, zeolite

INTRODUCTION

It is very well known, that specific structures give to zeolites properties which make them useful in many different and important applications, such as catalysis, ion-exchange, adsorption [1]. In order to search for a new or optimize/improve their performances in present applications, it is necessary to deepen the knowledge about all factors which influence process of their synthesis, and consequently properties of the final product.

Structural characterization is one of the most important steps in investigations and analysis of materials. One investigates precursors, samples taken during a process of preparation or final products (i.e. crystalline materials). Commonly, in zeolite investigations, methods of characterizations are: XRD, SEM, TEM, adsorption/desorption of N₂, AFM, to mention some of them. In our investigations we have additionally implemented PALS, as a method for the structural characterization. PALS is an established and well-proved method for structural investigations of various materials, extensively used for metals and alloys, semiconductors and different porous materials as well as zeolites [2, 3]. It relies on the measurement of positron lifetime from its birth in a source to annihilation with an electron inside the bulk of the sample. With this method it is possible to detect voids inside a material, their sizes and relative concentrations. Obtained information is valuable addition to the data obtained by other methods. In this work some of the results obtained by applying PALS in structural investigation of zeolites, zeolite precursors and materials obtained by synthesis of zeolites in the presence of a template for the formation of mesopores, will be shown and discussed.

EXPERIMENTAL

Zeolite materials and their precursors were prepared as explained in references 4, 5, 6 and 7. Generally, for precursors investigations silicate and aluminate components were mixed, obtained precursors (gels) were aged at room (RT) or higher temperatures, or ion exchanged if required [4, 5]. Crystalline zeolites were obtained by hydrothermal treatment of precursors [6]. Zeolite related materials were obtained by combining precursors with a template for the formation of mesopores, which were than hydro-thermally treated. The obtained products were

calcined [7]. Solid parts of the samples of prepared precursors or final crystalline zeolites and related materials, were separated from liquid phase, washed, dried, calcined if required, and then used for different characterizations. For PALS characterization two pellets of solid sample were prepared, additionally dried and mounted into sample chamber of the PALS experimental set-up, each from one side of the radioactive positron source. Detailed description of the PALS experimental set-up can be found in ref. 8.

RESULTS AND DISCUSSION

Row data obtained from PALS measurements were processed by LT v. 9 computer fitting program [9], and distributions of positron lifetimes and corresponding intensities, correlated to relative concentrations, were extracted. Positron lifetimes longer than approximately 0.7 ns were considered as long lifetimes and were related to ortho-positronium, *o*-Ps, long living positron-electron bound state. There could be several long living positron components with different lifetimes (τ_3 , τ_4 , τ_5) showing the presence of voids of different sizes in the material. These long lifetimes can be correlated to the approximate sizes of voids inside of the materials, and their corresponding intensity values to the relative concentrations of voids [10].

1. Zeolite precursors (influences of type of cations, way of preparation and ageing of the precursors)

PALS was used to investigate structural diversity inside precursors (gels) matrix in connections to presence of different cations (Na, K, Rb, Cs) and the way of their introduction into the matrix: directly or by ion exchange [4]. Obtained long lifetime components are shown in Table 1. It can be seen that τ_3 values in ion exchanged gels are all about 0.9 ns, while in directly prepared gels τ_3 are in range 0.94 to 1.30 ns. In directly prepared gels, each cation influenced formation of the precursor and in these samples some correlation to the size of present cation can be noticed. In ion-exchanged gels, gel matrix has been formed in the presence of Na cation, and cations entering and exchanging Na cation do not show very pronounced influence on formed structure. Long lifetimes τ_4 and τ_5 show that also larger voids are formed in the samples.

Table 1. Long lifetime positron components and corresponding intensities in ion-exchanged and directly prepared gels

Sample	Ion-exchanged gel			Directly prepared gel		
	τ_3 (ns) I3(%)	τ_4 (ns) I4(%)	τ_5 (ns) I5(%)	τ_3 (ns) I3(%)	τ_4 (ns) I4(%)	τ_5 (ns) I5(%)
Na gel	0.91±0.03	3.7±0.2	94±2	1.01±0.04	3.9±0.5	57±6
	12.6±0.6	1.06±0.08	2.74±0.05	9.6±0.3	1.1±0.1	1.75±0.07
K gel	0.89±0.03	3.8±0.3	66±5	0.94±0.07	3.2±0.4	104±8
	11.5±0.8	1.6±0.1	2.7±0.1	9.0±0.8	1.4±0.3	5.5±0.3
Rb gel	0.96±0.01	3.96±0.15	89±18	1.15±0.13	2.9 ±0.3	124±23
	11.65±0.08	1.21±0.03	1.6±0.2	5.4±0.5	1.8±0.4	3.4±0.4
Cs gel	0.94±0.09	2.7±0.4	52±7	1.30±0.07	5.0±0.4	62±3
	11±1	1.8±0.5	1.2±0.1	7.3±0.3	2.3±0.2	4.7±0.1

The results shown in Table 2 are obtained by applying PALS for structural investigation of freshly prepared and aged gels (5). It can be seen that in aged gels intensity values of positron

long lifetime components, are increasing in comparison to the freshly prepared gel. This can be connected to the increase of the number of structural entities inside matrix during ageing. This was additionally proved by hydrothermal treatment of those precursors. Product from freshly prepared gel contained smaller amount of larger crystals, compared to that obtained from aged gels. Gels aged for 48 hours at 40 °C, become fully crystalline, as shown by their XRD and FTIR results, and here highest concentration of voids has been detected by PALS.

Table 2. Long lifetime positron component and corresponding intensity in freshly prepared and aged gels

	STATUS OF GEL		
	Fresh	Aged at room temperature for 48 h	Aged at 40°C for 48 h
τ_3 (ns)	1.10 ± 0.07	1.1 ± 0.1	1.03 ± 0.07
I_3 (%)	5.6 ± 0.6	8 ± 1	12 ± 1

2. Zeolite crystallization and drying

During crystallization of LTA zeolite at 80 °C/4h, increase of intensity values of long positron lifetime components with rather constant lifetime values has been found, similar to the findings in aged gels, suggesting increase of order during crystallisation.

Although the same temperature regime was applied to all of the investigated zeolites, differences in positron lifetimes and intensity values have been found in experiment with drying of different types of zeolites [6]. These differences can be connected to the structural type and crystal size of the zeolite. For example (Table 3), much faster diffusion of water molecules in smaller crystals was accompanied by very large ($\tau_4 > 10$ ns) positron lifetimes. This shows that part of positrons reach the surface of the small crystal, escape from it, and annihilate in the voids between particles. Much larger voids between crystals compared to the voids inside the crystal are related to these very long positron lifetimes which were detected.

Table 3. Long lifetime positron components and corresponding intensity in FAU crystals

	Small FAU crystal				Large FAU crystal			
	τ_3 (ns)	I_3 (%)	τ_4 (ns)	I_4 (%)	τ_3 (ns)	I_3 (%)	τ_4 (ns)	I_4 (%)
RT	1.798 ± 0.008	13.8 ± 0.3	-	-	1.695 ± 0.004	12.3 ± 0.09	-	-
80 °C	2.26 ± 0.05	9.9 ± 0.1	12.5 ± 0.9	1.99 ± 0.06	2.23 ± 0.09	9.3 ± 0.2	5.7 ± 0.1	5.9 ± 0.3
100 °C	2.13 ± 0.03	9.1 ± 0.2	27.7 ± 0.6	2.56 ± 0.03	2.17 ± 0.06	10.2 ± 0.2	5.7 ± 0.1	5.6 ± 0.2
140 °C	1.91 ± 0.03	8.4 ± 0.2	32.1 ± 3.9	3.2 ± 0.4	2.26 ± 0.03	12.2 ± 0.1	6.27 ± 0.08	4.8 ± 0.1
180 °C	1.97 ± 0.03	8.2 ± 0.1	33.3 ± 2	3.5 ± 0.3	2.45 ± 0.05	11.8 ± 0.2	6.7 ± 0.2	4.6 ± 0.3

3. Formation of mesoporous materials from zeolite precursors

Using PALS, formation of mesoporous materials from zeolite precursors (original and modified) in the presence of a template for the formation of mesopores, was monitored [7]. In Table 4, long lifetime components are shown. τ_3 values and high intensity values in samples before and after synthesis point to presence of template in the material [11, 12] and τ_4 values and accompanied intensity values in samples after calcination point to the presence of voids

created by calcination and removal of template from the same material. τ_3 values and low intensity values in calcined samples also show that removal of the template was not complete.

Table 4. Long lifetime positron components and corresponding intensity in materials formed from original and modified gels in the presence of template for the formation of mesopores

Sample	a)		b)		c)	
	original	gel	modification-1		modification-2	
	τ_3 (ns)	τ_4 (ns)	τ_3 (ns)	τ_4 (ns)	τ_3 (ns)	τ_4 (ns)
	I_3 (%)	I_4 (%)	I_3 (%)	I_4 (%)	I_3 (%)	I_4 (%)
Before synthesis	4.05±0.02	28.3±0.3	3.21±0.01	24±1	4.28±0.01	25.9±0.5
	9.4±0.2	4.62±0.08	11.6±0.1	0.68±0.01	10.75±0.03	2.02±0.02
After synthesis	3.70±0.02	16.1±0.3	3.788±0.009	29±1	3.50±0.02	27±1
	10.3±0.1	1.08±0.02	14.47±0.03	0.80±0.01	11.7±0.1	0.74±0.02
After calcination	4.2±0.2	31.1±1.7	4.2±0.2	36.0±0.3	3.84±0.05	34.6±0.05
	3.86±0.08	11.0±0.4	1.81±0.03	11.20±0.07	2.46±0.02	12.47±0.02

CONCLUSION

In all shown and discussed cases of structural characterization of precursors or crystalline materials by applying PLAS, voids of different sizes and concentrations inside matrix have been detected. Their sizes and concentrations were different on the way of preparation or subsequent processing.

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