



Positronium lifetime measurements in micro- and mesoporous ferrisilicates

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ABSTRACT

Positron annihilation lifetime, Doppler broadening measurements have been used to study microporous FER and MFI structures containing framework substituted iron in different amounts. Mesoporous SBA-15 samples without and with iron introduced to the pore walls were also investigated by these methods. Mössbauer measurements have been accompanied to prove the extent of isomorphous incorporation of iron into the different structures. The results reveal a certain dependence of lifetimes on the various pore and channel sizes. Addition of iron does not influence significantly the observed lifetimes in FER microporous systems. However a slight decrease of lifetimes can be observed in the MFI samples. The effect of addition of iron in mesoporous SBA-15 system is more expressed. Supplement of iron also has an influence on the S parameter of Doppler broadening spectra.

1. Introduction

Porous structures can advantageously be studied with positronium annihilation measurements. Annihilation of para positronium is fast (125 ps), in contrast to the lifetime of ortho positronium (o-Ps) which is larger with three orders of magnitude (140 ns). If o-Ps interacts with electrons of the environment (“pick-off” annihilation) the observed lifetime becomes shorter. If o-Ps positronium is trapped inside porous structures the observed lifetime can be correlated with the size of cages and channels (Gidley et al., 2006; Jean et al., 2003). The 10–130 ns lifetime interval corresponds to 2–100 nm pore size range by the extended Tao-Eldrup approximation (Dull et al., 2001).

Beside the commonly used lifetime measurements, energy distribution around the 511 keV annihilation peak can also be measured by Doppler broadening method. Small variations in the signal shape may provide information on the interactions of o-Ps with valency and core electrons of the host matrix via the S (shape) and W (wing) parameters, respectively (Jean et al., 2003; Liskay et al., 2001). Usually relative tendencies are analyzed in S - W plots since selection of the considered ranges in Doppler spectra depends strongly on the experimental conditions (Kajcsos et al., 2009).

Pore sizes of microporous silicates (zeolites) and mesoporous substances are in the mentioned size range. Typical microporous structures (MFI and FER) are strictly crystalline, with interpenetrating channel systems with diameters of 0.45–0.55 nm (Baerlocher, 2001). Characteristic features of mesoporous MCM-41 and SBA-15 structures are their larger channel diameter (4–6 nm) and their partly amorphous pore wall structure (Schacht et al., 1998). Both of these types of

materials have achieved broad variety of applications, thus they have been widely characterized by o-Ps measurements, too (Goworek, 2014; Kajcsos et al., 2005). Combination of micro - and mesoporous structures, namely those with so-called hierarchical porosity can also be studied (Zubiaga et al., 2016). Studies on mesoporous substances (e.g. MCM-41) with positronium lifetime measurements are also reported (Zaleski et al., 2003).

Beside pure silica and alumina based porous structures, further ones containing additional transition metal ions substituted isomorphically into the framework are also widely used in the practice. Addition of the transient metal ion modifies the electron densities in the cages, thereby it may influence the lifetime of o-Ps positronium, too (Süvegh et al., 2001). Further on adsorption of gas molecules (nitrogen, oxygen and even water from humidity of air) takes easily place in cages of micro- and mesoporous substances, modifying thereby the actual size of cages (Cabral-Prieto et al., 2006; Kajcsos et al., 2007). Thus these measurements should usually be performed after evacuation. Iron modified MCM-41 with iron in the pore walls (Wiertel et al., 2013) as well as with Fe₂O₃ (Surowiec et al., 2010) or with mixed oxide Mn-ferrites (Wiertel et al., 2014) in the channels have also been characterized with the method.

Iron containing zeolites and mesoporous substances can advantageously be studied by another technique, with Mössbauer spectroscopy, too. This method provides information solely on the close environment of iron. Combination of the two techniques may strengthen the interpretation of data (Zaleski et al., 2003; Wiertel et al., 2013; Kajcsos et al., 1993).

In our previous publications, general aspects of studying porous

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media with positronium studies were discussed (Cabral-Prieto et al., 2006). Further on sorption and removal of adsorbed water in zeolites (Liszakay et al., 2001), and early stages of crystallization of zeolites (Bosnar et al., 2007) were also followed by the method. Preliminary results of positronium lifetime measurements on comparison of microporous FER, MFI with various iron contents and mesoporous SBA-15 plain silicate with its iron modified ferrisilicate counterpart have been reported recently (Dung et al., 2013). The microporous structures exhibit 2–20 ns lifetimes for o-Ps, whereas 4–52 ns lifetimes were found for mesoporous SBA-15 in correspondence with the expectations of the extended Tao-Eldrup model. Addition of iron decreased the lifetimes in Fe-MFI and in Fe-SBA in comparison to the corresponding plain porous silicates. Iron species in the microporous structures were identified by Mössbauer spectroscopy as well (Dung et al., 2013). The present report accounts on further studies on various iron modified microporous (Fe)-FER and (Fe)-MFI as well as on mesoporous plain and iron modified SBA-15. In particular, lifetime measurements are completed with determinations of S and W parameters from Doppler measurements, and a broader scope in interpretation is also provided. In situ Mössbauer spectra are also shown to identify the species of iron present in the mesoporous Fe-SBA.

2. Experimental

2.1. Samples

2.1.1. Microporous (type A) samples

Fe-FER samples with Si/T atomic ratio of 16 have been synthesized. T stands for the modifying ion substituted isomorphously to tetrahedral sites into the siliceous framework. In the first case, for Fe-FER sample, solely Fe was used, resulting in an average composition of $\text{FeSi}_{16}\text{O}_{34}$. In the second case, for (Al,Fe)-FER sample, both Al and Fe (in Al:Fe = 3 ratio) were introduced into the tetrahedral framework sites ($\text{FeAl}_3\text{Si}_{64}\text{O}_{136}$). Thus, the amount of iron was only $\frac{1}{4}$ th in the latter sample in comparison to the first Fe-FER. Further details of the synthesis and characterization can be found (Lázár et al., 1998).

The extent of isomorphous substitution with Fe and Al ions located in tetrahedral sites was significantly smaller for Fe-MFI samples than for the previous Fe-FER ones, Si/T exceeded 40 in each case. Si/Fe ratios are 50 and 100 for samples Fe-MFI-50 and 100, respectively. In other words, iron content was doubled in Fe-MFI-50 as compared to Fe-MFI-100. The dominant substituting ion was Fe, with addition of Al in 1/3 portion. Thus the average nominal compositions were $\text{AlFe}_2\text{Si}_{100}\text{O}_{206}$ and $\text{AlFe}_2\text{Si}_{200}\text{O}_{406}$ respectively. To provide the possibility for obtaining Mössbauer spectra at these low iron contents ^{57}Fe isotope was used for sample preparation. Further details of preparation and characterization are reported in (Fejes et al., 2003).

2.1.2. Mesoporous SBA-15 (type B) samples

SBA-15 was prepared by using mixture of P123 block copolymer, water, acidified with HCl. The siliceous pore structure was formed from gelation with tetra-ethyl-orthosilicate with subsequent hydrothermal treatment in an autoclave at 100 °C for 24 h, then filtered and dried at room temperature. The template was removed by calcination at 450 °C in oxygen for 5 h. The specific surface area of the product was $580 \text{ m}^2\text{g}^{-1}$, the average channel diameter was 5.7 nm as determined from BET measurements. Further details of preparation and characterization are described in the publications (Beck et al., 2008).

Fe-SBA-15 was prepared with Si/Fe ~65 ratio (approximate nominal composition $\text{FeSi}_{65}\text{O}_{132}$). The preparation was similar to that applied for the previous plain SBA-15 with addition of iron into the starting synthesis mixture. Namely, P123 block copolymer was dissolved in 1.9 NHCl, then $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was added to the solution. Further stages were similar to that applied for the synthesis of plain SBA-15. The specific surface area of the Fe-SBA-15 was $715 \text{ m}^2\text{g}^{-1}$, the average channel diameter was 8.6 nm. Further details of synthesis and char-

Table 1
List of samples.

| Type | Sample | Si/ Fe (at) | Si / Al (at) | Ref. |
|-----------------|----------------|-------------|--------------|------|
| Microporous (A) | A-Fe-FER | 16 | - | [20] |
| | A- (Al,Fe)-FER | 64 | 24 | [20] |
| | A-Fe-MFI-50 | 50 | 200 | [21] |
| | A-Fe-MFI-100 | 100 | 200 | [21] |
| Mesoporous (B) | B-Fe-SBA-15 | 65 | - | [23] |
| | B-SBA-15 | - | - | [22] |

acterization are presented (Lázár et al., 2004). List of samples is shown in Table 1.

2.2. Measurements

2.2.1. Lifetime (PALS) and Doppler (DBS) positronium measurements

In all PAS measurements the radioactive positron source has been sandwiched between two disk-shaped pieces of samples. Na-22 sources were used for both DBS and PALS measurements. The zeolite powder was pressed (0.3 GPa) into disks of 8–13 mm diameter and 1–1.5 mm thickness. In the PALS studies the samples were processed and prepared sandwiching the Na-22 source wrapped in Al foil. Samples and source were placed in a sample holder in an Al vacuum chamber. Adsorbed water was removed from the pores by a combined evacuation and heat treatment before the measurements performed at room temperature.

PALS measurements with low-activity (0.5–2 MBq) Na-22 source were performed. A fast-fast coincidence PALS was equipped with XP 2020 URQ photomultipliers and BaF₂ scintillators and NE111 plastic scintillator. Wide energy selection windows were set to enable high efficiency, still providing good time resolution (250 ps FWHM for 60-Co). The spectra were obtained by employing time-to-pulse height converter units, in case of simultaneous use of two of them allowing also the setting of different time ranges simultaneously. The data collection chains on the PALS consisted of standard ORTEC and TENNELEC units. The data collection took place with computer-based multichannel cards - the 16k Oxford Microfast products. The time calibration values for the various settings varied from 20.1 ps/ch up to 200.3 ps/ch, respectively. In each spectrum integral counts number at $2 \cdot 10^6$ were recorded. The time base of the PALS setup was 8192 channels. A good reproducibility of the results was found by recording spectra over several days and repeating the experiments. The lifetimes and relative intensities were also evaluated using the LT v.9 fitting program (Kansy, 1996). All PALS spectra were decomposed to four lifetime components.

In DBS technique the 511 keV annihilation energy, which is broadened by the Doppler shift by the total momentum of the positron-electron annihilation pair, is directly measured. The S parameter, which corresponds to positron annihilation with the valence electrons, is defined as the ratio of the central area of the 511 keV annihilation gamma ray peak to the total peak area. The W parameter, which corresponds to positron annihilation with the core electrons, is the ratio of the edge area of the DB peak to the total area electrons. In this DBS study the apparatus is typical and energies in the range of 40 keV–1.4 MeV were recorded by using a Canberra HPGe detector with 1.86 keV FWHM resolution at the 1.28 MeV line of positron source. A low-activity (0.5–2 MBq) Na-22 source were used. Each spectrum carried about 6 million counts.

2.2.2. Mössbauer measurements

Mössbauer measurements were performed by using a spectrometer using 1 GBq ^{57}Co source. Fe-FER, Fe-MFI and Fe-SBA samples were treated at different conditions (evacuation at 650 K, reduction in hydrogen at 620 K) in an in situ Mössbauer cell (Lázár et al., 1984). Most of spectra were collected at room temperature. Parameters were extracted by decomposing the spectra to components of Lorentzian line

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