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Positron annihilation lifetime in mesoporous silica MCM-41 at different vacuum levels

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Abstract

Positron annihilation lifetime spectra of MCM-41 and zeolite Y were measured at different vacuum levels. When the experiments were carried out in air, a very long lifetime component ($\tau_4 = 35\text{--}45$ ns, $I_4 = 15\text{--}20\%$) was observed for MCM-41, while the longest lifetime for zeolite Y was only 2–4 ns with an intensity of 15–25%. However, when the experiments were carried out in vacuum, the very long lifetime components could be observed for both samples, although with different intensities, $\sim 30\%$ for MCM-41 and $\sim 10\%$ for zeolite Y. For MCM-41 in air, the longest lifetime (τ_4) is ~ 42 ns, corresponding to the *ortho*-positronium (*o*-Ps) annihilation lifetime in MCM-41 cavities. This value is slightly longer but very close to the value of 39 ns, which was estimated by using a bouncing quantum particle model. These peculiar positron annihilation characteristics were explained by air quenching mechanism of *o*-Ps annihilation in MCM-41. It was suggested that because of the existence of the very long lifetime component even in air, positron lifetime spectroscopy could be a very useful tool for nondestructive measurement of the cavity size of mesoporous solids such as MCM-41.

1. Introduction

MCM-41 is an ordered mesoporous silica, which is very appealing as a host for both catalytic species and electronic species [1, 2]. In the studies involving porous solids, the determination of cavity size and its absorption properties are very important. With an assumption about the particular cavity geometry, the cavity size and cavity wall thickness of MCM-41 can be evaluated by using data of interplanar spacing and pore volume which are usually obtained from a routine XRD and adsorption characterization [3, 4]. HRTEM is also a powerful tool for elucidation of cavity geometry. To obtain a complete understanding of the cavity structure of MCM-41 more experimental techniques complementary to the aforementioned approaches are desirable. Positron annihilation lifetime spectroscopy (PALS) has been a powerful tool for investigation of voids in polymers [5, 6]. The very long lifetime components in positron annihilation lifetime spectrum are well correlated to the properties of voids or cavities in polymer. The void size can be evaluated from the lifetime value by using a well established

formula [7, 8]. PALS has also been successfully applied to other porous materials, such as zeolites [9–11]. Recently Ito has derived an equation to estimate the annihilation lifetime of *ortho*-positronium (*o*-Ps) in a cavity larger than 1 nm radius [12], which is just the case of MCM-41. This Japanese group has also done a pioneer experimental work on positron annihilation in MCM-41 and MCM-48 [13]. In this paper we report on the unusual positron annihilation lifetime characteristics of MCM-41 at different vacuum level and a proposed interpretation of the observed phenomenon.

2. Experiment

The MCM-41 powders were synthesized by a hydrothermal process. First, 0.75 g of cetyltrimethylammonium bromide (CTMBr) was diluted with 40 ml of water at 80 °C. Then 10.5 g of tetraethylammonium hydroxide (TEAOH) and 4.15 g of fumed silica were added and stirred for 2 h. The silica solution was moved to a Teflon autoclave and left at room temperature overnight. Next day the autoclave was moved into an oven and kept at 160 °C for 24 h. The obtained MCM-41 jelly was washed, filtered and dried at room temperature for 2 days. Finally, the jelly was heated to 550 °C and kept there for 9 h.

A zeolite Y sample is also used for comparison. All sample powders were pressed into 15 mm × 4 mm diameter pellets. A ²²Na source of about 30 μCi, sealed in Kapton film, was sandwiched by two pieces of identical samples.

Positron annihilation lifetime spectra were measured by a fast–fast coincidence system. The full width at half maximum for the ⁶⁰Co prompt curve at the ²²Na window condition was 350 ps, while the time scale was 0.2 or 0.4 ns/ch. All lifetime spectra were analysed by the computer program PATFIT. In general, four components were resolved with lifetime values of $\tau_1 = 0.15\text{--}0.25$ ns, $\tau_2 = 0.45\text{--}0.60$ ns, $\tau_3 = 2.5\text{--}6.0$ ns, $\tau_4 = 20\text{--}75$ ns. In order to get more reliable results for longer lifetime components, all data of channels before the peak in the lifetime spectra were omitted while τ_1 was fixed to 0.21 ns in all the following data fitting.

3. Results and discussion

The typical positron annihilation lifetime spectra for MCM-41 and zeolite Y samples measured in vacuum have very long tails indicating a very long lifetime (~70 ns), while the intensity of the very long lifetime of the MCM-41 spectrum is much higher than that of the zeolite Y spectrum (figure 1). When the samples were measured in air, the very long lifetime component for MCM-41 still existed while for zeolite Y it disappeared as shown in figure 1. This result is very peculiar. To our knowledge, when a solid sample measured in air, no lifetime component as long as ~40 ns with a strong intensity (>10%) has been reported. Many previous results of PALS in porous solids reported the existence of a very long lifetime component (20–80 ns), but the measuring conditions must be in vacuum. When the measurement was made in air, the intensity of the very long component must be relatively weak (<10%).

In general, positrons can form positronium in porous solids and annihilate with a very long lifetime. The positronium could form and annihilate in two different regions: the free space between powder particles and the inner space of the cavities of porous solids as shown in figure 2. Hereafter we will call these two regions outer space and inner space for simplicity. Both outer space and inner space could accommodate positronium formation and annihilation yielding a very long lifetime. It is difficult to distinguish these two origins of very long lifetime. For example, a very long lifetime of ~70 ns in zeolite Y measured in vacuum could be an average value of the lifetime of Ps in supercages and Ps in some more open space, e.g. the free

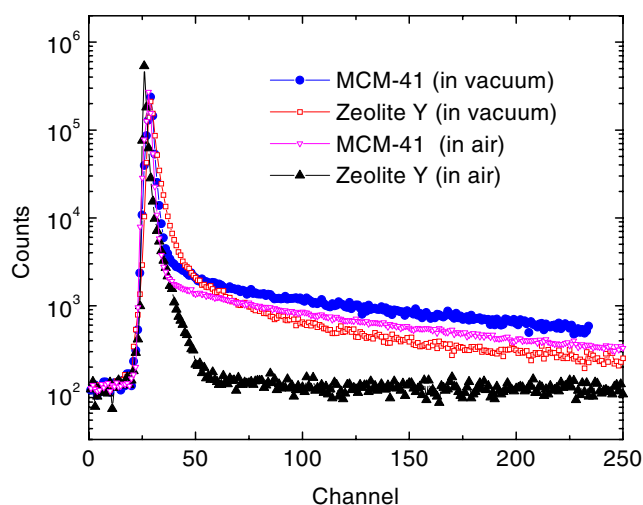


Figure 1. The typical positron annihilation lifetime spectra of MCM-41 and zeolite Y measured in vacuum. The time scale is 0.4 ns/ch. The lifetime and intensity values of the longest lifetime components (τ_4/I_4) in vacuum are 67 ns/28% and 39 ns/10% for MCM-41 and zeolite Y respectively, while the lifetime and intensity values of the longest lifetime components (τ_4/I_4) in air are 49 ns/16%.

Table 1. The four-component fitting results of positron annihilation lifetime spectra of MCM-41 measured at different vacuum level. χ^2 is the variance of the fit. The numbers in brackets mean errors in the units of corresponding last digits. For instance for τ_2 0.56(1) ns means (0.56 ± 0.01) ns.

Vacuum level (Pa)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	τ_4 (ns)	I_1 (%)	I_2 (%)	I_3 (%)	I_4 (%)	χ^2
1.5	0.210	0.56(1)	5.4(3)	65(1)	36(1)	31(1)	4.1(1)	28.8(2)	0.891
10	0.210	0.58(1)	6.2(3)	67(2)	36(1)	32(1)	4.1(1)	28.4(2)	1.225
10^2	0.210	0.58(1)	5.8(4)	64(2)	38(1)	30(1)	4.0(2)	27.6(2)	1.033
10^3	0.210	0.49(1)	2.9(2)	51(1)	37(2)	37(1)	4.0(2)	21.5(2)	1.155
10^5	0.210	0.49(1)	3.4(2)	42(1)	34(1)	41(1)	4.0(1)	20.5(1)	1.058

volume between small zeolite grain particles [10]. When a sample was measured in air, Ps in the open space between powder particles could be quenched by oxygen in air and annihilate in a shortened lifetime. In this case, the longest lifetime must be due to Ps annihilation in the cavities. Thus, the big difference between MCM-41 and zeolite Y shown in figure 1 must be due to the cavity size and structure differences between these two samples. Then the only explanation for figure 1 is that the mesoporous cavities of MCM-41 could contribute a very long and very strong positron lifetime (>40 ns) in air, while zeolite Y could not!

To get a closer observation of air quenching effects of positronium annihilation, lifetime spectra were measured at different vacuum levels. Four-component fitting results were listed in table 1.

Figure 3 shows the variation of τ_4 and I_4 as functions of the vacuum level. It can be seen from figure 3 that both τ_4 and I_4 decrease as pressure increases indicating the air quenching effects of positronium. As mentioned above, τ_4 is an average lifetime of Ps lifetime in cavities and outer space between powder particles. The decrease of τ_4 as pressure increasing means the Ps lifetime in outer space is longer than that in the cavities. From the variation of I_4 shown in

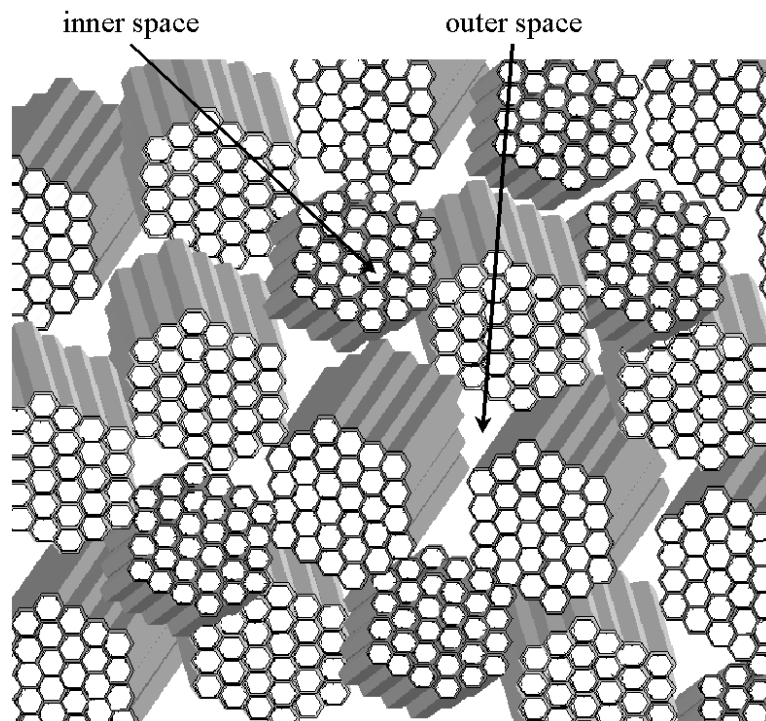


Figure 2. Two different regions in MCM-41 for positronium formation and annihilation: the free space between powder particles (hereafter we call this the outer space) and the inner space of the cavities. These spaces are wide enough to accommodate positronium formation and annihilation yielding very long lifetimes.

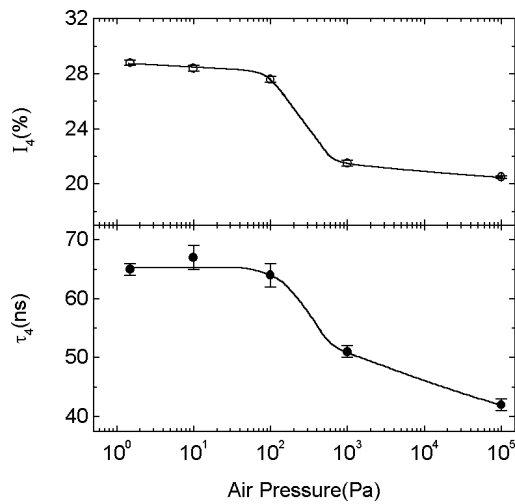


Figure 3. The parameters of the longest lifetime component in MCM-41 as functions of the vacuum level. τ_4 is the longest lifetime value and I_4 is its intensity. Both τ_4 and I_4 decrease as pressure indicating the air quenching effects of positronium.

figure 3 the intensity of the longest lifetime component contributed by the outer space between particles can be estimated to be 8%.

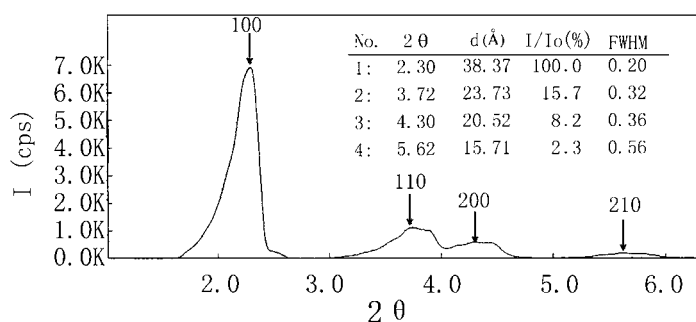


Figure 4. The x-ray diffraction of the MCM-41 sample used for the vacuum level dependent measurement. The radius of the cavities of the sample was estimated to be 1.9 nm.

In all PALS studies on porous solids it is important to understand how to correlate the lifetime values to the cavity sizes. According to Ito *et al* [12], the *o*-Ps annihilation rate in cavities is given by a sum of two fractional rates at the two annihilation regions; one is a pick-off annihilation of *o*-Ps with electrons of the cavity wall, and the other is an intrinsic annihilation process of *o*-Ps in a vacuum at the middle of the cavity, i.e.

$$\lambda = \lambda_{2\gamma}(1 - f(R)) + \lambda_{3\gamma} \quad (1)$$

where $f(R)$ is the probability that *o*-Ps wave packets do not interact with the electron layer at the surface of the cavity wall. $\lambda_{2\gamma}$ is the pick-off annihilation rate due to *o*-Ps wave packets penetrating into the electron layer of the wall. According to a rigid spherical potential, $\lambda_{2\gamma}$ is given in units of ns^{-1} by [7, 8]

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

where the thickness of the electron layer is fitted to be 0.166 nm for zeolites and other porous materials. From a geometrical consideration [3, 4], the radius of the cavity of the MCM-41 sample, R , can be estimated from XRD data shown in figure 4 as 1.9 nm. Taking $\Delta R = 0.166$ nm and a similar assumption as made in [12], the total annihilation rate of *o*-Ps in the MCM-41 cavities can be calculated as 39 ns by using equation 6(a) of [12]. This is very close to 42 ns, the τ_4 value measured in a low vacuum level listed in table 1.

The decrease of τ_4 by increasing air pressure can be contributed by the pick-off process between *o*-Ps and the molecules absorbed in the cavity. From the results one can see that the pick-off process of *o*-Ps by air molecules is very different in the cavity than in the outer space. In a cavity, *o*-Ps can only approach a particular absorbed molecule, most probably a nitrogen molecule that is not such an effective quenching species, while *o*-Ps in outer space has much more chance to collide with oxygen molecules, which have unpaired electrons and thus are more effective *o*-Ps quenching species. This means that when experiments were done in air, *o*-Ps annihilating in outer space will contribute a shortened lifetime (0.5 ns); while annihilation in the cavities will contribute to a very long lifetime. This gives us a hint that it is possible to use this existing very long lifetime even in air to study the cavity structures and cavity inner surfaces of different samples under atmosphere. Since in air, the contribution of outer space to τ_4 can be ruled out, all observed changes of τ_4 from sample to sample are mainly due to the cavities. Thus by measuring τ_4 and I_4 , much important information about the cavity size, the guest species intercalated into the cavities and the inner surface linings could be obtained.

4. Conclusions

Positron annihilation lifetime spectroscopy was used to study the cavity structure of MCM-41 in comparison with zeolite Y. Based on the positron annihilation spectra measured in different vacuum levels, several points can be concluded as follows.

- (1) A very long (>40 ns) and strong ($>10\%$) lifetime component can be resolved from the positron annihilation lifetime spectrum of MCM-41 measured in air. This component becomes even longer (~ 70 ns) when the measurement is carried out in vacuum. While in zeolite Y, this very long component can only be observed in vacuum.
- (2) The *o*-Ps quenching process by air in cavities of MCM-41 is very different from the process in its outer space. Because of the selectivity of adsorption, the *o*-Ps in cavities may not encounter effective quenching species like oxygen, and thus may survive for a much longer time than in air. This is the reason why a very long and strong lifetime component can be observed in MCM-41 even in air.
- (3) The lifetime value of the longest component for MCM-41 with cavity size of ~ 4 nm is ~ 42 ns when the measurement is made in air. The value is slightly longer but very close to that predicted by the bouncing quantum particle model by Ito *et al* [12].

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