Positron Annihilation Studies of Mesoporous Silica MCM-41

J F Williams[1], P Guagliardo[1], K Sudarshan[1], C Ranganathaiah[1], G Koutsantonis[2], N Hondow[2] and S Samarin[1]

[1]Centre for Antimatter-Matter Studies, School of Physics, The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia
[2]School of Chemistry and Biochemistry, The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia

E-mail: paul.guagliardo@uwa.edu.au

Abstract. Positron annihilation has been used to study the mesoporous silica MCM-41. Lifetime spectra of evacuated MCM-41 indicate a significant contribution from 3γ annihilation events with τ_4 = 116 ns and I_4 = 24.5 %. This is supported by measurements of the full energy distribution, where MCM-41 shows enhanced counts in the low energy region (below 511 keV) relative to a pure 2γ sample. MCM-41 was also studied under air and oxygen atmospheres. The presence of atmosphere has a significant effect on both the lifetime and Doppler patterns, with both the lifetime data (τ_4 and I_4) and the 3γ-fraction decreasing with increasing oxygen concentration. This is indicative of paramagnetic quenching of o-Ps by oxygen.

1. Introduction

Positron annihilation has been used to study MCM-41, a mesoporous silica composed of an array of non-intersecting hexagonal channels or pores of uniform size. This material has been extensively investigated for applications in catalysis due to its high surface area and structured array of pores [1]. In the following, we have utilised positron lifetime spectroscopy and Doppler broadening spectroscopy (registering the full energy distribution of annihilation radiation) to study MCM-41. We have compared the pore size determination from lifetime measurements with x-ray diffraction (XRD) data and have looked at the effects of atmosphere (vacuum, air and oxygen) on positron lifetime and Doppler broadening results.

2. Experimental

X-ray diffraction (XRD) studies indicated that the MCM-41 powders used had an ordered pore structure surrounded by amorphous pore walls with a uniform diameter of approximately 29 Å [2].

Lifetime spectra were recorded with BaF_2 detectors angled at 60°, and approximately 20 μCi of ^{22}NaCl sealed in Kapton foil was used as the positron source. The time dispersion of the lifetime spectrometer was 119 ps per channel (1 μs TAC range), and the time resolution was approximately 380 ps owing to the large stop windows employed, extending into the Compton region so as to register 3γ-annihilation events. Each spectrum contained at least 4 million counts and good reproducibility of the spectra was found upon reprocessing of the samples. Data analysis was carried out using PAScual version 1.30 [3]. Doppler broadening measurements were recorded simultaneously, with the HPGe detector sufficiently removed from the source; the energy resolution of the detector was approximately 1.5 keV at 511 keV.

The samples were heated at 150 °C under vacuum for ~ 48 hours prior to measurement in order to remove free water. After this time they were briefly exposed to air (for less than 10 minutes) while packed with the source and then transferred to the main vacuum system for positron annihilation measurements. Experiments were performed at a base pressure of 4×10^{-1} Torr. The vacuum chamber was equipped with a gas handling system to admit air (atmospheric gas) and oxygen (ultrahigh purity).

3. Results and Analysis

Figure 1 shows annihilation gamma-ray spectra measured using a HPGe detector for samples of MCM-41 (evacuated) and copper. The spectra have been normalised to the area of the 1.274 MeV peak. The MCM-41 spectrum shows enhanced counts to the left of the 511 keV photo peak relative to copper, and to the right of the photo peak the counts coincide. The reduced photo peak intensity and enhanced low energy background for MCM-41 suggests a significant contribution from o-Ps self-annihilation into 3γ-quanta, as for 3γ -annihilation, the energy distribution of the individual quanta is continuous and increases monotonically up to 511 keV [4]. The fraction of 3γ events ($f_{3\gamma}$) can be quantified by comparing the relative integral counts in the 511 keV peak for a 3γ-sample ($A_{2\gamma}$) with that of a pure 2γ–sample ($A^0_{2\gamma}$) (typically a metal sample to exclude Ps formation) [5]. The relative number of positrons annihilating in the 3γ channel can be expressed as

$$f_{3\gamma} = 1 - A_{2\gamma}/A^0_{2\gamma}$$

This measure gives a value of 23.5 % for MCM-41.

Lifetime measurements were also performed on MCM-41 and similarly indicate a significant 3γ contribution. The spectrum could be decomposed in terms of four lifetime components. The shorter components τ_1 and τ_2 are associated with p-Ps and free positron annihilation. The total intensity of these components comprises 74.9% of the spectrum. The longer components of τ_3 = 7.1 ns and τ_4 = 116 ns, with respective intensities of 0.9% and 24.3%, correspond to o-Ps annihilation. These results differ somewhat from MCM-41 studies described in the literature [6, 7]; however, there were significant differences in the sample synthesis as well as experimental parameters, such as the vacuum level.

The shorter of these, τ_3, could be attributed to o-Ps pick-off annihilation in nano regions within the silica matrix; the rectangular Tao-Eldrup (RTE) model [8] attributes a spherical pore diameter of 12 Å to this lifetime value. The long lifetime τ_4 and its high relative abundance suggest a high proportion of 3γ events. When τ_4 = 116 ns is converted to a pore size using the RTE model, the values obtained are significantly larger than the cavity size determined by XRD measurements (adopting a square channel geometry, a side length of 169 Å is obtained). This could indicate that annihilations occur predominantly in the free space between powder particles rather than in the inner space of the cavities. It is difficult to distinguish between these two possible contributions for the very long lifetime, and τ_4 could be the average of positronium annihilation in the channels and in the outer space.

The influence of atmosphere was also investigated. Lifetime spectra are shown in figure 2 for MCM-41 recorded under vacuum and in air and oxygen atmospheres (≈ 1 atm). It can be seen that the presence of atmosphere leads to drastic changes in the lifetime spectra. For each case the spectrum could be analysed in terms of four components (see table 1). The long lifetime component τ_4 decreases by a factor 1.7 in the presence of air and by a factor of 3.4 in the presence of oxygen, relative to the vacuum value. The intensity of this component I_4 also decreases with increasing oxygen concentration, with the weighting shifting mostly to I_1, associated partly with p-Ps. This is indicative of paramagnetic quenching by oxygen [9]. The adsorption of gas molecules can also lead to a reduction in the apparent pore size; furthermore, the alteration of the chemical nature of the pore surface due to gas adsorption can change the probability of pick-off annihilation in each collision. The positronium quenching rate constant of oxygen is reported to be 0.023 ± 0.003 ns^{-1} atm^{-1} [10, 11]. Taking the partial pressure of oxygen in air to be 0.2 atm and the same quenching constant to be valid for oxygen present in the mesopores, the rate constant in air would be 0.0046 ns^{-1} atm^{-1}. If we calculate the quenching rates from the measured lifetimes we obtain 0.0059 ns^{-1} atm^{-1} for air and 0.020 ns^{-1} atm^{-1} for oxygen. The value

for oxygen is within the uncertainty of the literature result; however the rate for air is higher than the expected value.

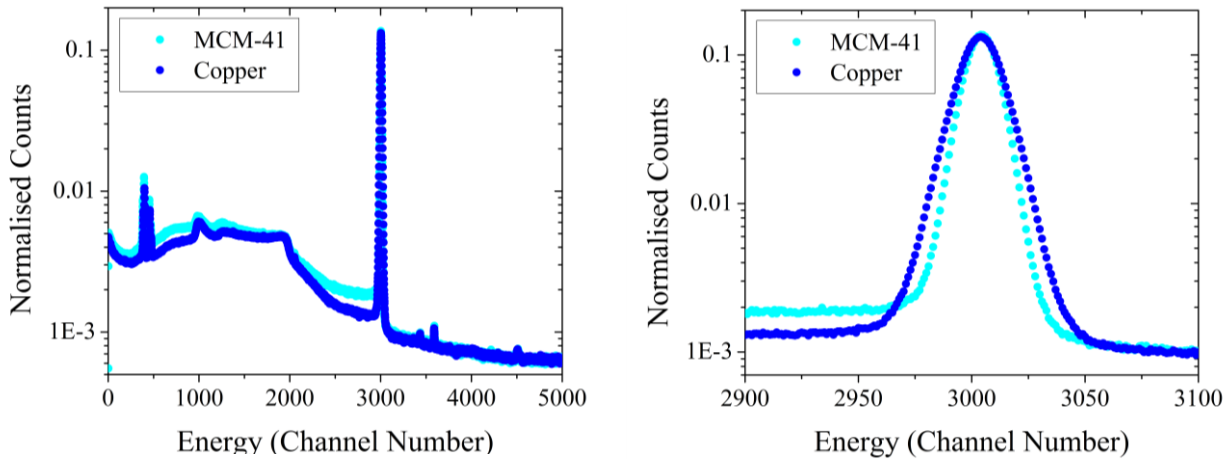

Figure 1. Energy spectra of MCM-41 and Copper recorded with a HPGe detector.

However, the enhancement of the annihilation rate caused by air has shown a dependence on pore size [11]; this is likely due to the absorption of air molecules on the pore walls, and for the case of small pores the number of surface adsorbed molecules has been shown to exceed the number of free molecules in the volume of the pore [12]. This dependence is depicted in the right panel of figure 2 where the quantity λ_{air}-λ_{vac} is plotted for polymeric and silica samples containing spherical pores of differing sizes; a decrease in λ_{air}-λ_{vac} is seen with increasing pore radius. The value of λ_{air}-λ_{vac} for MCM-41 is also plotted as a green triangle in figure 2 and is somewhat below the trend depicted by this data. This could suggest a differing trend for samples containing regular channels; however the result of He et al. [6] for MCM-41 coincides with the data.

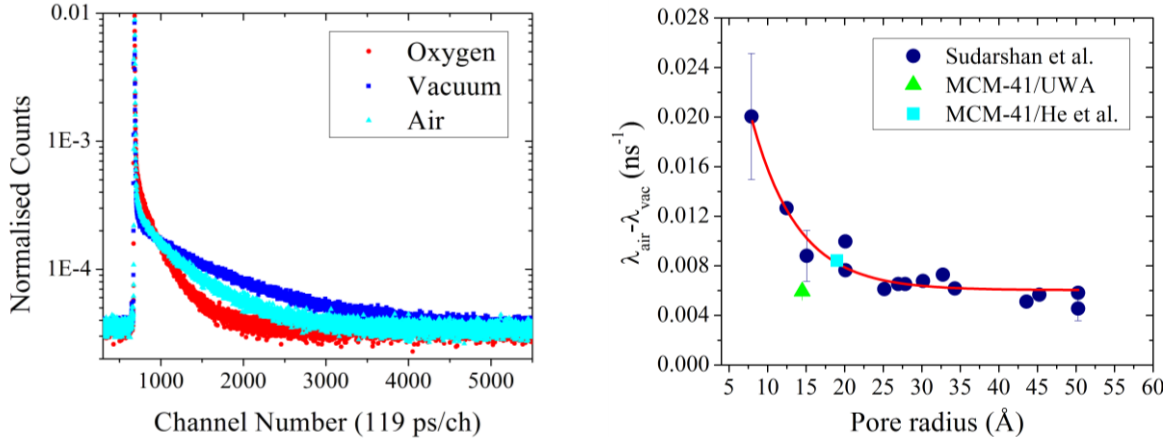

Figure 2. Left: Lifetime spectra of MCM-41 recorded under vacuum and in oxygen and air atmospheres (the peaks extends to about 0.1); right: λ_{air}-λ_{vac} vs. pore size; the blue dots are the results of Sudarshan et al. [11], the cyan square is data from He et al. [6], and the green triangle is the MCM-41 data from this study.

Annihilation gamma-ray energy spectra for the three atmospheres were also recorded and the intensity in the Compton region was found to decrease with increasing oxygen concentration, indicating a decrease in the 3γ contribution due to paramagnetic quenching by oxygen. This is evidenced by the 3γ fraction (given in table 1) which decreases with increasing oxygen concentration, signalling the

conversion of o-Ps to p-Ps. Nitrogen was also studied and gave comparable results to those recorded under vacuum with only a slightly reduced 3γ fraction at 20.49%. This is consistent with literature results which show that nitrogen is not a strong positronium quencher.

Table 1. PALS fitting results for MCM-41 recorded in vacuum and in air and oxygen atmospheres; $f_{3\gamma}$ calculated from energy spectra

	Vacuum	Air	Oxygen
τ_1 (ps)	139 (2)	129 (2)	132 (2)
τ_2 (ps)	443 (2)	446 (2)	445 (2)
τ_3 (ns)	7.3 (0.2)	8.4 (0.2)	7.3 (0.2)
τ_4 (ns)	116 (0.3)	68.7 (0.3)	34.5 (0.2)
I_1 (%)	42.7 (0.2)	46.9 (0.3)	49.1 (0.3)
I_2 (%)	31.7 (0.2)	33.7 (0.3)	32.9 (0.4)
I_3 (%)	1.0 (0.1)	1.9 (0.1)	3.4 (0.1)
I_4 (%)	24.5 (0.1)	17.3 (0.1)	14.5 (0.1)
χ^2	1.085	1.056	1.082
$f_{3\gamma}$ (%)	20.5 (0.1)	10.3 (0.1)	4.2 (0.1)

4. Conclusions

Lifetime spectra of evacuated MCM-41 indicated a significant contribution from 3γ annihilation events with lifetimes exceeding 100 ns with high intensity. This is supported by measurements of the full energy distribution, where MCM-41 shows enhanced counts in the low energy region relative to a copper sample. The presence of atmosphere was found to drastically change the positron lifetime and Doppler patterns due to paramagnetic quenching by oxygen molecules.

References

[1] Taguchi A and Schüth F 2005 *Micro. and Meso. Mater.* **77** 1
[2] Hondow N S, Koutsantonis G A, Nealon G L and Saunders M 2012 *Micro. and Meso. Mater.* **151** 264
[3] Pascual-Izarra C, Dong A W, Pas S J, Hill A J, Boyd B J and Druumond C J 2009 *Nucl. Instrum. Meth. Phys. Res. A* **603** 456
[4] Ore A and Powell J L 1949 *Phys. Rev.* **75** 1696
[5] Liszkay L, Kajcsos Z, Duplâtre G, Lázár K, Pál-Borbély G and Beyer H K 2001 *Mater. Sci. For.* **363** 377
[6] He Y J, Zhang H Y, Chen Y B, Wang H Y and Horiuchi T 2001 *J. Phys.: Conden. Mat.* **13** 2467
[7] Zaleski R, Wawryszczuk J and Goworek T 2007 *Rad. Phys. Chem.* **76** 243
[8] Dull T L, Frieze W E, Gidley D W, Sun J N and Yee A F 2001 *J. Phys. Chem. B* **105** 4657
[9] Klobuchar R L and Karol P J 1980 *J. Phys. Chem.* **84** 483
[10] Celitans G J, Tao S J and Green J H 1964 *Proc. Phys. Soc.* **83** 833
[11] Sudarshan K, Dutta D, Sharma S K, Goswami A and Pujari P K 2007 *J. Phys.: Conden. Mat.* **19** 386204
[12] Zaleski R and Sokół M 2011 *Mater. Sci. Forum* **666** 123