Positron Annihilation Studies of Mesoporous Silica MCM-41

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Abstract. Positron annihilation has been used to study the mesoporous silica MCM-41. Lifetime spectra of evacuated MCM-41 indicate a significant contribution from $3\gamma$ annihilation events with $\tau_4 = 116$ 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 $2\gamma$ 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 ($\tau_4$ and $I_4$) and the $3\gamma$-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 \cite{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 \cite{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 $3\gamma$-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 \cite{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 $4 \times 10^{-1}$ 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 peak. The MCM-41 spectrum shows enhanced counts to the left of the 511 keV photo peak relative to MCM-41 (evacuated) and copper. The spectra have been normalised to the area of the 1.274 MeV photon peak.

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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 $\lambda_{\text{air}} - \lambda_{\text{vac}}$ is plotted for polymeric and silica samples containing spherical pores of differing sizes; a decrease in $\lambda_{\text{air}} - \lambda_{\text{vac}}$ is seen with increasing pore radius. The value of $\lambda_{\text{air}} - \lambda_{\text{vac}}$ 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: $\lambda_{\text{air}} - \lambda_{\text{vac}}$ 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 $3\gamma$ contribution due to paramagnetic quenching by oxygen. This is evidenced by the $3\gamma$ 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 $3\gamma$ 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 |
|---|---|---|
| & $\tau_1$ (ps) & $\tau_2$ (ps) & $\tau_3$ (ns) |
| Vacuum & 139 (2) & 443 (2) & 7.3 (0.2) |
| Air & 129 (2) & 446 (2) & 8.4 (0.2) |
| Oxygen & 132 (2) & 445 (2) & 7.3 (0.2) |
| & $\tau_4$ (ns) & $I_1$ (%) & $I_2$ (%) |
| Vacuum & 116 (0.3) & 42.7 (0.2) & 31.7 (0.2) |
| Air & 68.7 (0.3) & 46.9 (0.3) & 33.7 (0.3) |
| Oxygen & 34.5 (0.2) & 49.1 (0.3) & 32.9 (0.4) |
| & $I_3$ (%) & $I_4$ (%) & $\chi^2$ |
| Vacuum & 1.0 (0.1) & 24.5 (0.1) & 1.085 |
| Air & 1.9 (0.1) & 17.3 (0.1) & 1.056 |
| Oxygen & 3.4 (0.1) & 14.5 (0.1) & 1.082 |
| & $f_3\gamma$ (%) |
| Vacuum & 20.5 (0.1) |
| Air & 10.3 (0.1) |
| Oxygen & 4.2 (0.1) |

4. Conclusions
Lifetime spectra of evacuated MCM-41 indicated a significant contribution from $3\gamma$ 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.

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