

Adsorption effects on positronium behavior in Y zeolites

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Zeolites are aluminosilicate minerals commonly used as commercial adsorbents, catalysts and molecular sieves thanks to their framework of sub-nanosized cages, cavities and channels. Ortho-positronium (o-Ps) is a well-recognized porosimetric probe and chemical probe for adsorption, pore filling and surface that has been extensively used to characterize pore size, connectivity and surface properties of porous materials including zeolites [1]. Our recent studies showed that the o-Ps behaviour significantly depends on the solid acidity of zeolite pore surfaces [2,3]. However, it remains unclear how o-Ps interacts with changes in the chemical state of pores under different absorption conditions. Here, Ps formation and annihilation were measured in Y zeolites adsorbed in various environments to investigate changes in the physico-chemical surface properties of pores.

Y zeolites with Si/Al ratios between 2.6 and 40 were moulded into 3-mm-thick tablets and dehydrated in vacuum at 185 °C for 2 h. Positron annihilation lifetime spectroscopy (PALS) measurements were carried out using a ²²Na source sandwiched between two identical samples under controlled environments (Ar, N₂, H₂O). PALS measurements in vacuum were conducted using the slow positron beam at AIST [4] with an incident positron energy of 15 keV. Analysis of the lifetime spectra was conducted by fitting with the sum of four lifetime components. The third (τ_3) and fourth (τ_4) components are related to o-Ps pick-off annihilation in the pores and “almost free” o-Ps annihilation in the interparticle free space. The fraction of o-Ps intrinsic annihilation ($f_{3\gamma}$) was evaluated by measurements of the full energy distribution (FED) of the annihilation radiation using a high-purity Ge detector.

τ_3 showed a dependence on the Si/Al ratio under all environments, which was understood to be the effect of the change in the number of Brønsted acid sites on the pore surfaces. The presence of adsorbates reduced τ_3 with respect to the value measured in vacuum and polar adsorbents, i.e. water, were found to have the greatest effect. This effect was ascribed to the suppression of o-Ps diffusion due to molecular adsorption in the pores. τ_3 measured upon water adsorption was consistent with the lifetime calculated from the size of the β -cage using the Tao-Eldrup model. τ_4 in the water-adsorbed state showed a lifetime reduction >25 ns compared to the value measured in vacuum and matched the size of the α -cage. The FED measurements in the N₂ atmosphere revealed a not negligible fraction of o-Ps self-annihilation. However, $f_{3\gamma}$ was significantly reduced after exposure to the atmosphere and consequent adsorption of moisture from the air. This confirmed that upon water adsorption almost all o-Ps annihilated by pick-off interaction.

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