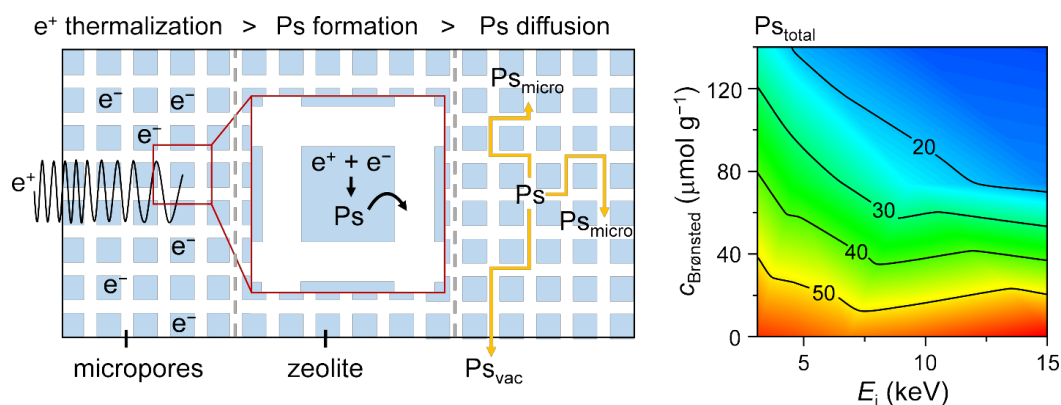


## Quantifying the impact of acidity on positronium formation and annihilation in zeolitic materials

R. Warringham<sup>1</sup>, L. Gerchow<sup>1</sup>, D. A. Cooke<sup>1</sup>, P. Crivelli<sup>1\*</sup>, J. Pérez-Ramírez<sup>1\*</sup>

<sup>1</sup>ETH Zurich

Positron annihilation lifetime spectroscopy (PALS) demonstrates unique sensitivity towards elucidating the connectivity of pore networks in zeolitic materials, which is based on the diffusional behavior of metastable *ortho*-positronium (*o*-Ps) species formed *in situ* upon positron implantation.<sup>1</sup> Chemical interactions between *o*-Ps and acid sites in a solid have been widely postulated to perturb the purely kinetic response.<sup>2</sup> However, the specific impact of the nature and amount of acid sites on the lifetime and intensity of different *o*-Ps components, and the implications for porosity analysis, have not been quantified. By studying a series of ZSM-5 (MFI structure) samples with tailored crystal size and Si:Al ratio, we map the dependence of the amount ( $Ps_{\text{total}}$ ) and fractional distribution ( $Ps_{\text{micro}}$ ,  $Ps_{\text{vac}}$ ) of *o*-Ps measured on the concentration of Brønsted acid sites and the implantation depth of positions (**Figure 1**). By modeling the possible mechanisms of interaction, we show that the presence of Brønsted acid centers most significantly affects the thermalization and delocalization of *o*-Ps, while the impact on diffusion and correspondingly on  $Ps_{\text{micro}}$  and  $Ps_{\text{vac}}$  is negligible. The study of commercial ZSM-5 samples confirms the generality of the findings and permits elucidation of the crystal size-dependent nature of kinetic and acidity effects. The impact of Brønsted acid sites can be eliminated by neutralization through exchange with  $\text{Na}^+/\text{K}^+$  ions. The negligible role of Lewis acid sites is confirmed from the study of a large-crystal Sn-MFI zeolite. By utilizing a controlled synthesis approach we are able to better account for the chemical interaction of *o*-Ps with acid centers, providing critical insights for the determination of pore quality in zeolites by PALS.



**Figure 1** Schematic of the formation, diffusion, and annihilation of *o*-Ps within a zeolite and correlation of  $Ps_{\text{total}}$  with the concentration of Brønsted acid sites and positron implantation depth.

[1] a) M. Milina, S. Mitchell, P. Crivelli, D. Cooke, J. Pérez-Ramírez, *Nat. Commun.* **2014**, 5, 3922. b) J. Kevin, S. Mitchell, M. Sterling, R. Warringham, T. C. Keller, P. Crivelli, J. Jagiello, J. Pérez-Ramírez, *Adv. Funct. Mater.* **2016**, 26, 5621.

[2] a) V. L. Goldanskii, V. G. Firsov, *Annu. Rev. Phys. Chem.* **1971**, 22, 209; b) W. F. Huang, D. C. Huang, P. K. Tseng, *Catal. Lett.* **1994**, 26, 269.