Unveiling CO_2 chemisorption mechanisms in porous adsorbents via surface-enhanced NMR: *quo vadis*?

Luís Mafra
CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.
Email: lmafra@ua.pt

Finding efficient ways to mitigate the ever-increasing amounts of anthropogenic CO_2 emissions is one of the biggest challenges of the century. To this end, solid sorbent materials are actively being sought for CO_2 capture technologies. Because of their significantly lower regeneration cost, compared to liquid absorbents, amine-modified porous silicas (AMPS) are among the most promising CO_2–adsorbents for replacing the decades-old liquid amine scrubbing technology. In contrast to many other solid adsorbents, AMPS are "moisture-tolerant" and selectively chemisorb CO_2 from low-concentration mixtures, important features for operating under large-point CO_2 emission source conditions.

The nature of CO_2 species interacting with porous surfaces determines the gas sorption capacity/kinetics, selectivity, stability, and regenerability. However, an atomic-level understanding of the CO_2-AMPS sorption process remains elusive, hindering our ability to design improved sorbents. The lack of advanced spectroscopic studies, tailored to elucidate the structure of adsorbed gas species, has also been a major bottleneck for further progresses in understanding the physical chemistry of gas-solid interfaces. Adapting spectroscopic tools to the study of confined species, interacting with porous surfaces, is not trivial. Herein, I will show that ssNMR is unique as it can act as a bulk or surface site-selective technique to study material surfaces of 'amorphous' AMPS porous adsorbents.

This presentation will quickly overview my previous research achievements and seeding ideas that provided the spur to embark on my ERC project. The last research advancements, recently obtained in my group, towards a better understanding of these CO_2-sorbent materials, will be showcased. The power of ssNMR techniques, computational methods and smart materials modification can be combined to unravel the complex nature of CO_2-adducts formed at AMPS surfaces, under controlled atmospheric conditions. Details on the rather controversial formation mechanism of moisture-induced CO_2 species are provided as water is a key component in flue gas streams, hypothesized to enhance CO_2 sorption capacity, and playing a major role in CO_2 speciation. The interconversion between distinct chemisorbed CO_2 species, under wet and dry conditions, is quantitatively assessed by ssNMR in silica sorbents grafted with amines possessing distinct bulkiness. It will be shown that ssNMR can detect proton-transfer mechanisms and validate the formation of different amine aggregation states in functionalized silicas; as well as assign various hydrogen-bonded CO_2 species that may occur upon formation of bicarbonate, carbamic acid and alkylammonium carbamate ion pairs.

This presentation will end by describing the main approaches devised to overcome the challenges that lie ahead in my ERC-COG project, aiming to find synergies with CIQUS-USC researchers.

Luís Mafra

Short bio-sketch

Address: Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
e-mail: lmafra@ua.pt
Scopus ID: 8877889600
ORCID: https://orcid.org/0000-0003-1028-8354
Homepage: http://www.ciceco.ua.pt/LuisMafra

Luís Mafra. b 1978, is currently a Principal Researcher and Manager of the solid-state NMR facility at CICECO - Aveiro Institute of Materials, University of Aveiro, Portugal. In 2006, he obtained his *PhD* from University of Caen (Laboratoire de Catalyse et Spectrochimie), France & University of Aveiro, working in solid-state NMR spectroscopy. During this period, he developed NMR methodologies to study the structure of hybrid materials using 1H high-resolution CRAMPS NMR techniques and methods to observe quadrupolar nuclei. In 2011 he was a *Postdoctoral* fellow at Max-Planck-Institut für Polymerforschung, Mainz, Germany. Published ca. 80 SCI research papers and 5 book chapters and gave *ca*. 60 (invited) talks at conferences (mostly international). Mentored 15 post-docs, 2 PhD students and 8 Msc+9 project students. PI of 9 R&D projects (*ongoing*: 3; *concluded*: 6), which received ~5.6 M€, funded by national (FCT), and European agencies. Since 2010, he also has been involved in technology transfer and collaborative research with various private companies.

Received various honors & awards, including: 2019 - European Research Council (ERC) Consolidator Grant; 2014 - promoted to Principal Researcher under the national "Investigator FCT" competitive program; 2014 - Adjunct Senior Lecturer honorary title, Sydney University (Australia); 2012 - Research excellence fellowship, Asturian region (Spain); 2006 - recipient of Celestino da Costa/Jean Perrin prize; 2009 - António Xavier Bruker prize. He is a member of the editorial board of Solid-state NMR (Elsevier) and regular reviewer of projects from governmental funding agencies of different countries.

Present Research Interests. Combination of solid-state NMR techniques with XRD and computational methods to study: intermolecular interactions in small molecule pharmaceuticals and heterogeneous porous catalysts and CO_2-sorption mechanisms in porous material's surfaces.