EUROPEAN SYNCHROTRON RADIATION FACILITY

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Application for beam time at ESRF – Experimental Method

This document should consist of a **maximum** of **two A4 pages** (including references) with a minimal font size of **12 pt**.

Proposal Summary (should state the aims and scientific basis of the proposal) :

We are applying for beam time to elucidate the structure of a MOF-MOF core-shell, in search of better resolution unattainable with conventional crystallographic methods. The engineered nanostructured material under study is a ZIF-8 core- ZIF-7 shell with SOD topology, where the shell controls the access of guest molecules into the core. In this work from ZIF-8 nanoparticles and, by following in-situ the synthesis of ZIF-7 shell with synchrotron radiation; we would have a better understanding of the transition of one MOF to the other and the coexistence of both. This core-shell structure with tunable microporosity (pore apertures of 3.0Å for ZIF-7 vs. 3.4 Å for ZIF-8) and different hydrophobicity will facilitate the production of highly homogeneous mixed matrix membranes, improving dispersion and interaction with the polymer due to its better interfacial contact for gas separation applications. Specifically, this ZIF-7/ZIF-8 core shell structure will be focused on pre-combustion CO_2 capture (H_2/CO_2). The proximity of their pore dimensions to H_2 kinetic diameter (2.9 Å) makes them ideal for enhancing membranes selectivity.

Scientific background :

Metal-organic frameworks (MOFs) are a fascinating type of porous solids synthesized with high specific surface areas, tunable pore sizes, shapes, and functionalities. These hybrid materials are made of metal ions or clusters joined to organic linkers which act as a bridge between metal centers [1]. ZIFs (zeolitic imidazolate frameworks) are a subclass of MOFs characterized by presenting zeolite framework topologies which combine high surface areas with exceptional chemical and thermal stabilities [2].

In our laboratory we have experience in the synthesis of diverse nanostructured porous materials to be embedded within a polymer in the form of mixed matrix membranes for improving the gas separation performance of the polymer membranes [3-5]. Nowadays MOFs are among the engineered type of porous solids more widely used [5-7] and the challenge consists in the creation of more sophisticated nanostructures by the combination of two different materials whose functionalities are complemented. For that two types of fillers of different nature have already been added in the same hybrid membrane (silica-MOF [8], or zeolite-MOF [9]), but also more sophisticated nanostructured materials such as core-shell type of structures have been created with the purpose of improving the interaction among filler-polymer phases to enhance the overall membrane performance. A shell of silicalite-1 was created by using ordered silica spheres as template core; [10] and silica-ZIF-8 core-shell spheres with ordered meso-microporosity [11] were applied for natural- and bio-gas upgrading. In both cases, silica microspheres were employed to create the selective shell.

Experimental technique(s), required set-up(s), measurement strategy, sample details (quantity...etc) :

In this study ZIF-8 and ZIF-7 powders (of ca. 100 nm) without any handling risk will be prepared in our laboratory by solvothermal synthesis, following by washing, centrifugation and drying. These materials will be used to follow the synthesis of the core-shell formation in-situ at ESRF´s facilities. For ZIF-7/8 core-shell synthesis ZIF-8 powder is in contact with ZIF-7 ligand (benzimidazole) in the proper reaction conditions to be crystallized in a DMF solution. A powder-liquid reaction cell developed in SpLine [12] will be used following the advice of the BM25 beamline stuff. Figure 1 shows the XRD patterns of ZIF-8, ZIF-7 powders and the core-shell ZIF-8/7 material (synthesized in excess of ligand vs. ZIF-8, 15:1, at 30 ºC for 24 h) where peaks related to ZIF-7, in comparison with ZIF-8, are marked in *. No enough counts to have a good resolution with our XRD source can be depicted. In addition, thermogravimetric analysis (Figure 2) indicates that the degradation of the ligand occurs at an intermediate temperature from ZIF-8 and ZIF-7, pointing out the coexistence of two types of ligands within the same core-shell structure.

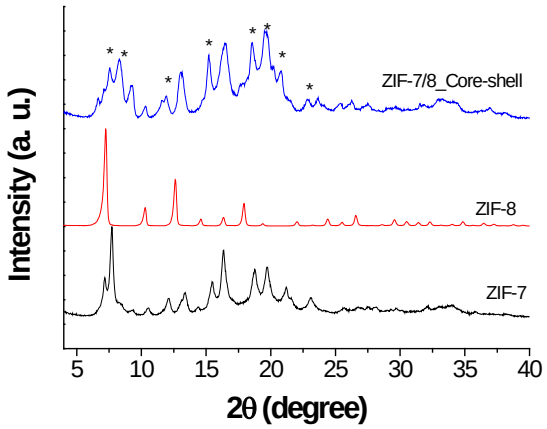

Figure 1. XRD spectra of ZIF-8, ZIF-7 and ZIF-7/8 core-shell (2.5-40º; scan speed 0.03º/s).

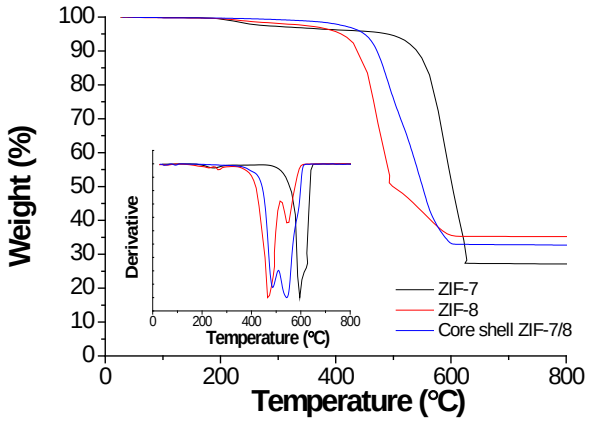

Figure 2. Thermogravimetric analysis of ZIF-8, ZIF-7 and ZIF-7/8 core-shell.

Beamline(s) and beam time requested with justification :

The synthesis of the core-shell by post-synthetic modification of ZIF-8 will be evaluated in-situ to find out the structure transition. Synchrotron radiation will be mandatory for this type of heterogeneous process, where one of constituents is liquid requiring high photon flux as very high resolution. With the aim of optimizing the core-shell type of structure, experiments with different excess of ligand (1/15, 1/7.5 and 1/4) at two different temperatures (30 and 90 ºC) for 3-4 h each in DMF reaction medium are planned. Besides, we would like to study the reversibility of the process forming ZIF-8/7 core-shell structures leading to a lower pore size shell, also with the aim of improving the overall membrane performance.

Results expected and their significance in the respective field of research :

By following the core-shell synthesis in-situ we expect to have a better resolution of the diffraction peaks and gain insights into the changes in crystallinity in the MOF transition and a kinetic study. The results obtained in synchrotron will be correlated and compared to the data obtained by the characterization techniques available at the University of Zaragoza (XRD, SEM, FIB, TEM, TGA-DTA, DSC, FTIR, NMR and XPS) to improve the knowledge on the synthesis properties and applications to form mixed matrix membranes, but also in the domains of adsorption or catalysis. One or two publications are expected.

References

[1] Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* 295 **(2002)** 469-472.
[2] Park, K. S.; Ni, Z.; Cote, A. P.; Choi, J. Y.; Huang, R. D.; Uribe-Romo, F. J.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M.*PNAS* 103 **(2006)** 10186-10191.
[3] Zornoza, B., Irusta, S., Téllez, C., Coronas, J. *Langmuir* 25 **(2009)** 5903-5909.
[4] Zornoza, B., Téllez, C., Coronas, J. J. Membr. Sci. 368 **(2011)** 100-109.
[5] Sánchez-Laínez, J., Zornoza, B., Mayoral, Á.; Berenguer-Murcia, Á., Cazorla-Amorós, D., Téllez, C. Coronas. J. *J. Mater. Chem. A*. 3 **(2015)** 6549.
[6] Zornoza, B., Martinez-Joaristi, A., Serra-Crespo, P., Tellez, C., Coronas, J. *Chem. Commun.* 47 **(2011)** 9522-9524.
[7] Zornoza, B., Tellez, C., Coronas, J., Gascon, J., Kapteijn, F. *Microporous Mesoporous Mater.* 166 **(2013)** 67-78.
[8] Valero, M., Zornoza, B., Téllez, C., Coronas, J. *Microporous Mesoporous Mater.* 192 **(2014)** 23-28.
[9] Zornoza, B., Seoane, B., Zamaro, JM., Téllez, C., Coronas J. *ChemPhysChem* 12 **(2011)** 2781-2785.
[10] Zornoza, B., Esekhile, O., Koros, WJ., Téllez, C., Coronas, J. *Sep Purif Technol* 77 **(2011)** 137-145.
[11] Sorribas, S. Zornoza, B. Téllez, C., Coronas J. *Chem. Commun.* 48 **(2012)** 9388-9390.
[12] Ferrer, P., da Silva, I., Heyman, C., Rubio-Zuazo, J., Castro, G R. *J. Physics: Conference Series* 425 **(2013)** 132001.