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Upgrading of polystyrene waste by photocatalytic cleavage in the presence of oxygen

(https://adum.fr/as/ed/voirproposition.pl?print=oui&matricule_prop=46913)

It is currently estimated that, worldwide, more than 300 million tons of plastics are produced per year **[1]**, often for short-term use, which implies the generation of large quantities of waste. To tackle this problem, mechanical recycling of plastics is the most developed method, but this is not satisfactory due to the lower quality of the recycled materials. The recovery by chemical processes is on the other hand much more promising but it requires for polymers, like polystyrene, to cleave C-C and C-H bonds. This can be done by pyrolysis but the related costs are rather high. Another approach, more economically interesting, consists in upgrading polystyrene by oxidizing pathways, the best being to use dioxygen as a reagent. It is then necessary to control the reaction in order to obtain selectively benzoic acid. Recent literature has shown a number of studies dealing with the deconstruction of $C(sp^3)$-$C(sp^3)$ bonds in alkyl aromatic compounds and even polystyrene under oxygen with the assistance of photocatalysts under mild conditions (room temperature and atmospheric pressure of O_2). Simple metal salts, such as $FeCl_3$ **[2]** or dyes, acting as organo-photocatalysts **[3]**, are used. One example even involves *para*-toluene sulfonic acid **[4]** which, by forming adducts with polystyrene, would be responsible for the photo-activation of O_2.

The present research project aims at developing organo-photocatalysts supported on mesoporous silica. From a mechanistic point of view, the selective hydroperoxidation of the C-H bonds in alpha position of the aromatic rings in polystyrene by oxygen in the singlet state has been postulated. It is then interesting to note that it has been shown several times, in the literature, that anchoring of dyes onto silica can minimize aggregation phenomena existing in solution and therefore improve the production of singlet oxygen **[5,6]**.

The host team has a strong experience in the development of oxidation catalysts, in particular for the cleavage of C-C bonds with applications initially in petrochemistry and also in the context of the valorisation of lignin **[7]**. In general, it has also acquired an important know-how related to the grafting of organic molecules and/or complexes on mesoporous silicas. This thesis subject will be based on these two pillars.

The candidate must have a master's degree or an engineering degree with a specialization in materials and an interest in catalysis or more generally in sustainable development. Experience in polymer characterization techniques may be considered a valuable asset.

References:

[1] Plastics - the Facts 2020 by PlasticsEurope - Issuu **[2]** M. Wang *et al*, ChemSusChem **2021**, 14, 5049; G. Zhang *et al*, Chin. J. Chem., **2021**, 39, 3225 **[3]** M. Forchetta *et al*, Catalysts, **2023**, *13*, 220 **[4]** T. Li *et al*, ACS Catal. **2022**, *12*, 8155 **[5]** J. Xu *et al*, New J. Chem., **2023**, 47, 1861 **[6]** C. Mendoza et al, Environ. Sci. Pollut. Res., **2021**, 28, 25124 **[7]** L. Al Hussaini *et al*, Dalton. Trans. **2021**, 50, 12850 ; S. Armenise *et al*, Journal of Analytical and Applied Pyrolysis **2021**, 158, 105265 ; L. Al-Hussaini *et al*, Materials **2020**, 13, 812 ; L. El Aakel *et al*, J. Mol. Catal. A: Chem. **2004**, 212, 171 ; L. El Aakel *et al*, Chem. Commun. **2001**, 21, 2218; M. Balas *et al*, Journal of CO_2 Utilization **2022**, 65, 102215 ; R. Villanneau *et al*, Inorg. Chem. **2013**, 52, 2958; N. Balistreri *et al*, J. Mol. Catal. B: Enz. **2016**, 127, 26 ; W. Zhao *et al*, J. Porous Mater. **2008**, 15, 139.