UFR DE CHIMIE

PhD thesis offer

Conversion of eggshell waste into efficient catalysts through exsolution of non-noble-metals

Eggshell waste is among the most abundant waste materials coming from food processing technologies. Despite the unique properties that both its components (the shell itself and its membrane) possess, it is very often discarded without further use.[1] The present project aims at converting eggshells into particularly active catalysts for CO_2 methanation and CH_4 dry reforming, two important processes in the frame of pollution control and renewable energies.[2] Eggshells will be treated to obtain catalyst precursors to which low-cost catalytically relevant non-noble-metals will be added. The resulting materials will be further treated to trigger a phenomenon that is currently a hot topic in heterogeneous catalysis, namely metal exsolution.[3] This phenomenon is so far mostly reported for perovskite-type oxides. It consists in the migration of metals incorporated on bulk sites of the perovskite towards the surface under a reducing atmosphere (H_2 flow, for instance) at temperatures above 800 °C. It leads to metal nanoparticles with a size depending on the latter temperature, which are socketed on the surface, thus unable to agglomerate. On the other hand, we recently showed at LRS that exsolution of metals can also occur within another type of materials, namely metal-substituted hydroxyapatites ($Ca_{10-x}M_x(PO_4)_6(OH)_2$, M: Ca^{2+}-substituting metal).[4] In that case, the exsolution occurs at only 450 °C and leads to highly dispersed metal sites at the surface rather than to nanoparticles. Thus, depending on the materials, the exsolution of metals seems to lead to different configurations of the metal sites, each of these configurations being more or less appropriate depending on the catalytic process of interest. In the present project, the idea is to exploit this new tool, exsolution, to control the configuration of catalytically active sites on eggshell-derived oxides to render the latter particularly efficient and thereby contribute to shifting heterogeneous catalysis into circular economy.[5] In order to establish properties-exsolution-activity relationships, the physico-chemical properties of the materials will be characterized by a wide range of techniques (ICP-AES, XRD, N_2 physisorption, IR, Raman and UV-Vis spectroscopies, XPS, H_2-TPR, TEM and SEM microscopies, etc.). The phenomenon of exsolution as well as the catalytic mechanisms will be investigated in real time through *in situ*/*operando* Raman – UV-Vis – IR spectroscopies. *Operando* monitoring refers to the simultaneous recording of spectroscopic data on the working catalyst to follow structural changes and adsorbed species, and the catalytic performance (reactant(s) conversion, selectivity to the desired product(s), stability).[6]

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Information on the application process: https://ed397.sorbonne-universite.fr/fr/future-doctorate-candidate/ed397-competition.html

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