

'Physique et Chimie des Matériaux' – ED 397 – année 2022

PhD project for funding, to send by 28/02/2022 to

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Research unit (full name + acronym) : Laboratoire de Réactivité de Surface

Team if applicable :

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Nber of PhD under supervision 0.5 ☐

Participation to supervisor training? ☐ no ☒ Year

Co-supervisor :

HDR? ☐ select Position : ☐ select

Tel

email :

Research unit :

International co-supervision ? ☐ select

Keyword 1 : Utilization of CO₂

Keyword 2 : Catalytic materials

Keyword 3 : Capture of CO₂

Keyword 4 : Process intensification

Select co-funding programme if applicable : ☐ select

Project title : Catalytic materials for the valorization of CO₂ from diluted sources

Project Description :

Context : CO₂ can be used to make fuels or fine chemicals thanks to the development of ever more efficient catalysts but very few of them are able to work starting with low concentrations of CO₂. Often, CO₂ has to be captured before [1]. Materials with high specific surface area such as alkaline earth oxides or hybrid materials involving amino groups are investigated for CO₂ adsorption. But, more interestingly, materials allowing both CO₂ adsorption and its catalytic transformation would allow significant energy savings. In this work, we will focus our attention on the valorization of carbon dioxide through its reaction with epoxides (formation of cyclic carbonates as polymer precursors) in liquid phase. A gas phase transformation, i.e. the conversion of methane and carbon dioxide into carbon monoxide and dihydrogen (Dry Reforming of Methane (DRM)) will also be envisaged through collaborative projects. In these different reactions, metals such as NiO (DRM) or MnIII (CO₂ cycloaddition) will be involved for catalysis.

Background : While significant advances have been made in the synthesis of pure silica or silica doped with hetero-elements, reported textural properties of basic oxides (MgO, CaO, etc.) are much lower [2]. In contrast, recent work has shown that mesoporous magnesium carbonate with very good textural properties (Upsalite [3]) and even calcium carbonate can be easily synthesized. This has led us to use those carbonates as precursors of mesoporous CaO after an appropriate decarbonation heat treatment. This approach, which avoids the use of porogen agents, was tested in a preliminary work at the Laboratoire de Réactivité de Surface [4]. After nickel incorporation during the synthesis of the calcium carbonate precursor, the resulting material, Ni@CaO, proved to be an efficient catalyst in the dry reforming reaction of methane. Generally, the activity of heterogeneous catalysts is very dependent on the preparation of well-dispersed metallic nano-phases.

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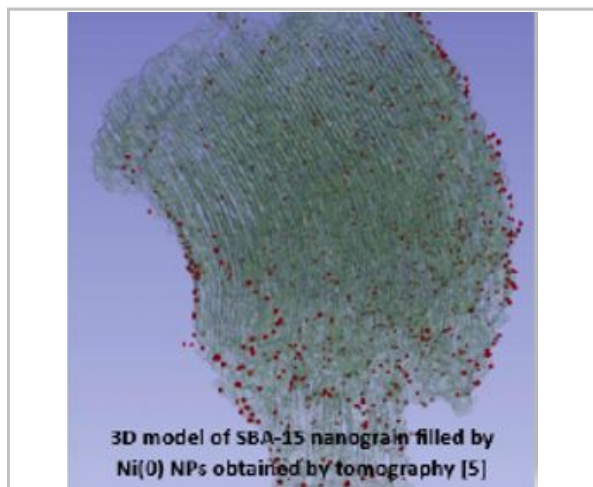
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A very promising approach to control the size of supported metal nanoparticles relies on the preparation of colloidal suspensions, ideally in water, and then on their deposition onto an inorganic carrier [5]. This synthesis strategy is not applicable in the case of zero-valent non-noble metals, such as nickel. Recently, we have shown that colloidal nickel(II) carbonate or hydroxycarbonate can help to overcome the instability of nickel(0) nanoparticles in water [6]. Once deposited on a silica support (Figure), these colloidal particles were thermally converted into phyllosilicate (NiII@SiO_2) and then, with dihydrogen, into metallic nickel without losing the initial control of the particles size, thus leading to Ni@SiO_2 catalysts more active in the dry reforming of methane than those resulting from a simple impregnation of silica with nickel(II) salts.

Aim of the project: On the basis of those previous experiences, we propose to study more systematically the use of mesoporous or nanometric carbonates for the synthesis of heterogeneous catalysts. The challenges to be faced concern the characterization of the species at the different steps of synthesis, the control of the conditions of the thermal conversion of carbonate supports (MgCO_3 , CaCO_3) into oxide supports or carbonate colloidal particles of Mg, Ca, Ni(II) or Mn(III) into oxide or metallic nanoparticles. Ni(II) will be introduced and reduced in the case of the DRM catalyst while, for the activation of the epoxides, Mn(III) will be kept in its oxidation state, thus affording the Lewis acid sites required. In this approach, no external halides (Lewis bases), usually employed for the ring opening of the epoxide in the CO_2 cycloaddition, will be involved. Instead, we will count on the surface carbonates obtained by the interaction of CO_2 with the basic oxide. Indeed, we earlier showed, in homogeneous conditions, that soluble hydrogenocarbonates can replace non-environmentally friendly halides [7]. Surface amino propyl functions are also expected to be useful candidates for CO_2 adsorption through the formation of carbamates, also able to induce the ring opening of epoxides [8]. Both approaches will be compared.

This thesis topic mainly requires skills in inorganic chemistry and physicochemical characterization methods. We are looking for a candidate who is motivated by catalysis and has a basic knowledge in organic chemistry or chemical engineering. He/she will be trained to the synthesis of inorganic porous materials, their characterization as well as catalysis tests under pressure and their analytical control by GC-MS.



References

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- [3] J. Forsgren et al, PLOS ONE, 2013, 8, e68486.
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- [7] C. Carvalho Rocha, T. Onfroy, F. Launay et coll, J. Catal., 2016, 333, 29.
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