



CHINA SCHOLARSHIP COUNCIL

Appel à projets

Campagne 2022

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Title of the research project :

Catalytic materials for the valorization of CO₂ from diluted sources

Thesis supervisor (HDR) :

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Research Unit

Name : Laboratoire de Réactivité de Surface

Code (*ex. UMR xxxx*) :

UMR 7197

Doctorate School

Thesis supervisor's doctorate school (candidate's futur

doctoral school) : PHYSICS AND CHEMISTRY OF MATERIALS Doctoral School 397

PhD student currently supervised by the thesis supervisor (number, year of the first inscription) :

1 (co-tutelle 50%) from 2020 (1st year)

Description of the research project

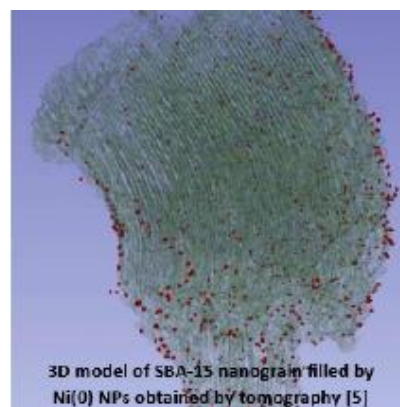
Context

Nowadays, carbon dioxide emitted in the atmosphere is considered as an alternative feedstock. 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, usually through absorption processes with aqueous amines that tend to decompose upon repeating cycles [1]. **Inorganic materials based on alkaline earth oxides or hybrid materials involving amino propyl substituents with basic properties and high specific surface area allowing CO₂ adsorption are highly desired. 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) 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 Ni⁰ (DRM) or Mn^{III} (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 (Al, Ti, etc.), 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 basic mesoporous oxides after an appropriate decarbonation heat treatment ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$). This approach, which avoids the use of porogen agents, was tested in a preliminary work at the Laboratoire de Réactivité de Surface [4], thus allowing calcium oxide with a specific surface area of around 15 m².g⁻¹, a value which may appear low but which is, with no optimization, higher than the average of the values listed in the literature. After nickel incorporation during the synthesis of the calcium carbonate precursor, the resulting material, Ni@CaO, proved to be a particularly efficient catalyst in the dry reforming reaction of methane. Basic sites in that reaction are helpful to reduce side reactions such as coke formation.

Generally, the activity of heterogeneous catalysts is very dependent on the preparation of well-dispersed metallic nano-phases. 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 unfortunately not applicable in the case of zero-valent non-noble metals, such as nickel, cobalt and iron, unless colloidal suspensions prepared in an organic medium are used. Recently, still in the case of Ni, 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 nickel oxide or nickel phyllosilicate (Ni^{II}@SiO₂) and then, with dihydrogen, into metallic nickel without losing the initial control of the particles size, thus leading to Ni@SiO₂ 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, within the framework of this PhD project, 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 (MgCO_3 , CaCO_3 , NiCO_3 , CoCO_3 , ...) into oxide or metallic nanoparticles, the choice of the stabilizing agents for the synthesis of colloidal carbonates or hydroxycarbonates.

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 here on nucleophilic species such as 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.

About the candidate

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. He/she will be trained to the synthesis of inorganic porous materials, their routine characterization (N_2 physisorption, XRD, TEM, TGA, ...) as well as catalysis tests under pressure and their analytical control by GC-MS.

References

- [1] Amine degradation in CO_2 capture. I. A review. C. Guedard, F. Launay et al, *International Journal of Greenhouse Gas Control*, **2012**, 10, 244.
- [2] Synthesis of non-siliceous mesoporous oxides. D. Gu et al, *Chem. Soc. Rev.*, **2014**, 43, 313.
- [3] A Template-Free, Ultra-Adsorbing, High Surface Area Carbonate Nanostructure. J. Forsgren et al, *PLOS ONE*, **2013**, 8, e68486.
- [4] Investigation of new routes for the preparation of mesoporous calcium oxide supported nickel materials used as catalysts for the methane dry reforming reaction. F. Launay et coll., *Catal. Sci. Technol.*, **2020**, 10, 6910.
- [5] Colloids for Catalysts: A Concept for the Preparation of Superior Catalysts of Industrial Relevance. J. Quinson et al, *Angew. Chem.*, **2018**, 130, 12518.
- [6] Aqueous nickel(II) hydroxycarbonate instead of nickel(0) colloids as precursors of stable Ni-silica based catalysts for the dry reforming of methane. F. Launay et coll., *Catal. Commun.*, **2020**, 138, 105953.
- [7] Experimental and theoretical evidences of the influence of hydrogen bonding on the catalytic activity of a series of 2-hydroxy substituted quaternary ammonium salts in the styrene oxide/ CO_2 coupling reaction. C. Carvalho Rocha, T. Onfroy, F. Launay et coll, *J. Catal.*, **2016**, 333, 29.
- [8] Advantages of covalent immobilization of metal-salophen on amino-functionalized mesoporous silica in terms of recycling and catalytic activity for CO_2 cycloaddition onto epoxides. M. Balas, F. Launay, et coll., *Eur. J. Inorg. Chem.*, **2021**, 1581.