

**MASTER DE CHIMIE DE PARIS CENTRE - M2S2**  
**Proposition de stage 2021-2022**  
**Internship Proposal 2021-2022**

**Parcours type(s) / Specialty(ies) :**

- Chimie Analytique, Physique et Théorique / *Analytical, Physical and Theoretical Chemistry* :  
 Chimie Moléculaire / *Molecular Chemistry* :  
 Chimie et Sciences Du Vivant / *Chemistry and Life Sciences* :  
 Chimie des Matériaux / *Materials Chemistry*:  
 Ingénierie Chimique / *Chemical Engineering*:

**Laboratoire d'accueil / Host Institution**

Intitulés / *Name* : Laboratoire de Réactivité de Surface  
 Adresse / *Address* : Tour 33/43, étage 3  
 Directeur / *Director (legal representative)*: Pr H. PERNOT  
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**Equipe d'accueil / Hosting Team :**

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 Responsable équipe / *Team leader* : F. LAUNAY / S. BOUJDAY  
 Site Web / *Web site* : <http://www.lrs.upmc.fr/en/personal-page-of-researchers/franck-launay.html>  
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*Internship period* \* : January, 31<sup>st</sup> to July, 1<sup>st</sup> 2022

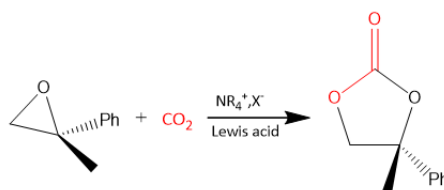
**Title**

**Use of supported inorganic carbonates as catalysts for the preparation of cyclic organic carbonates from epoxides and CO<sub>2</sub>**

**Scientific Project (maximum 1 page) :**

**1. Description of the project**

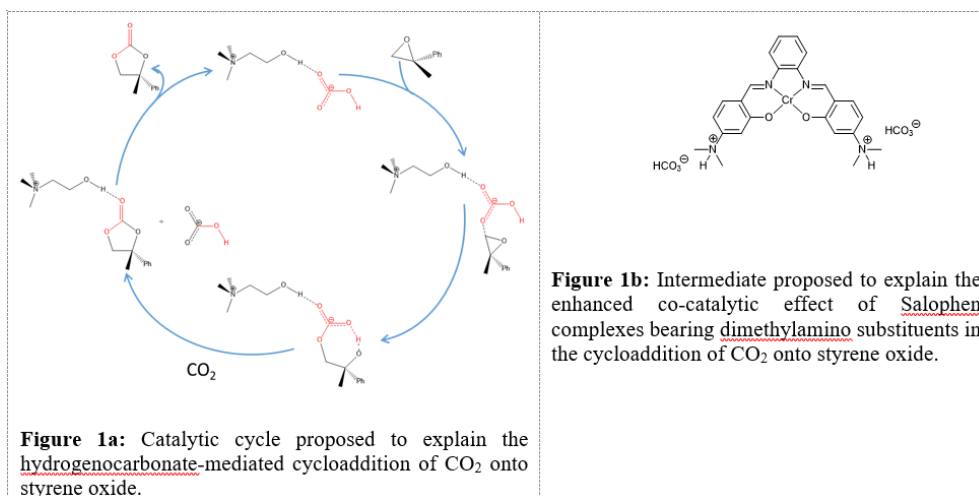
Cyclic carbonates can be prepared by the reaction of epoxides (e.g. styrene oxide) with carbon dioxide in the presence of catalytic amounts of a Lewis base (usually halides of quaternary ammonium salts) that opens the oxirane ring, and a Lewis acid (co-catalyst) in charge of its activation [1,2]. However, halides are not environment friendly catalysts and the use of alternative Lewis bases has to be investigated.



\* min. 5 mois à partir du 31 janv 2022 / *min. 5 months not earlier than January, 31st 2022.*

Fin de stage au plus tard le 15/07/2022 ou le 30/09/2022 (dates de validation de diplôme). / *End of internship at the latest July 15, 2022 or Sept. 30, 2022 (dates of graduation).*

We showed earlier, with the help of theoretical calculations, that hydrogenocarbonates of the same quaternary ammonium salts can be interesting candidates (Figure 1a) [3]. Similarly, we have observed recently that Salophen metal complexes (used as Lewis acids) bearing tertiary amine substituents are more efficient co-catalysts than other Salophen metal complexes [4]. Again, the improved activity was attributed to the *in-situ* formation of hydrogenocarbonates upon CO<sub>2</sub> capture by the tertiary amine (Figure 1b).



The present work aims at developing supported inorganic carbonates [5] and to use them as Lewis bases in cooperation with metal complexes. These carbonates will be obtained by the interaction of CO<sub>2</sub> with grafted tertiary amines or mesoporous basic oxides. In the longer term, these catalytic systems should be useful for the upgrading of diluted sources of CO<sub>2</sub> such as flue gases [6].

## 2. Specific techniques or methods

**Synthesis: Strategy n°1:** Synthesis of mesoporous silica-type materials, then co-grafting of tertiary amine functions and metal complexes. / **Strategy n°2:** Synthesis of mesoporous basic oxides, then incorporation of metal complexes.

**Characterization** of the structural (XRD) and textural (N<sub>2</sub> physisorption) properties of the materials as well as the composition (X-ray fluorescence, TGA) and basic properties (FTIR, CO<sub>2</sub> chemisorption).

**Catalytic tests** in autoclave and analytical follow-up by GC-MS.

## 3. References

- [1] *Heterogeneous catalysts for cyclic carbonate synthesis from carbon dioxide and epoxides*. M. North *et coll.*, *Current Opinion in Green and Sustainable Chemistry*, **2020**, 100365.
- [2] *Advantages of covalent immobilization of metal-salophen on amino-functionalized mesoporous silica in terms of recycling and catalytic activity for CO<sub>2</sub> cycloaddition onto epoxides*. M. Balas, F. Launay, R. Villanneau *et coll.*, *Eur. J. Inorg. Chem.*, **2021**, 1581.
- [3] *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<sub>2</sub> coupling reaction*. C. Carvalho Rocha, T. Onfroy, J. Pilmé, A. Denicourt-Nowicki, A. Roucoux, F. Launay, *J. Catal.* **2016**, 333, 29.
- [4] *Procédé catalytique durable pour la formation “one-pot” de carbonates cycliques par oxydation d’alcènes et cycloaddition de CO<sub>2</sub>*. Thèse Matthieu Balas, Sorbonne Université, **2021**.
- [5] *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.
- [6] *Amine degradation in CO<sub>2</sub> capture*. I. A review. C. Gouedard, F. Launay *et al*, *International Journal of Greenhouse Gas Control*. **2012**, 10, 244.