

I- Scientific context of project

Context: Hydrogen utilization is one of the keys to the development of a low-carbon economy, but H₂ storage and transportation is a technical lock that remains to be lifted to really develop H₂ use. Indeed, H₂ is currently stored and transported as compressed gas (high pressure conditions) or liquid (low temperature conditions) which incur high containment costs and concerns about safety and boil-off. Liquid Organic Hydrogen Carriers (LOHC) are probably one of the most appealing solutions to lift this technical lock: LOHC are organic compounds that can absorb and release a high weight fraction of hydrogen through chemical reactions, making therefore possible H₂ storage and transport under ambient conditions (e.g. using existing pipelines, figure 1). However, for a future industrial use of LOHCs, these organic molecules must meet precise criteria:

-first the loaded and unload LOHCs (LOHC⁺ and LOHC⁻) must respect important physical characteristics such as to be liquid or with a low melting point, a high boiling point, a high thermal stability but also a low toxicity. They should also, ideally, be sustainable and not based on the petroleum industry¹. Moreover, the LOHC must have a high gravimetric hydrogen content and high volumetric hydrogen storage capacity.

-Second, their catalytic hydrogenation (exothermic, high H₂ pressure, moderate temperature) and dehydrogenation (endothermic, high temperature, moderate H₂ pressure) should be performed using inexpensive catalysts based on affordable metals. Indeed “classical” hydrogenation catalysts are mostly based on critical metals (mostly noble metals) and recent **reviews on LOHCs¹ have pointed out that new efficient catalysts using non-noble metals working at lower temperature have to be developed**. Metallic particles of 3d transition metals such as cobalt, nickel, and iron or alloys of these three metals, appear to be very interesting candidates, as they have the potential to develop activities and selectivities similar to those of noble metals.

Aim: Thus, with this project, we aim to develop the use of **emerging Liquid Organic Hydrogen Carrier (LOHC) based on nitrogen containing compounds^{2,3}** and more precisely primary amine/nitrile pairs, starting with model alkylamine such as oleylamine (for which an activity in dehydrogenation of cobalt NPs has already been established by Partner 2 and 3⁴) and extending to diamines/dinitriles such as the 1,5-diaminopentane/1,3-dicyanopropane pair, together with **new, affordable, energy-efficient and cyclable catalysts based on cobalt, nickel and iron (bi)metallic nanoparticles**, either **colloidal or supported** on silica material to increase their stability and cyclability.

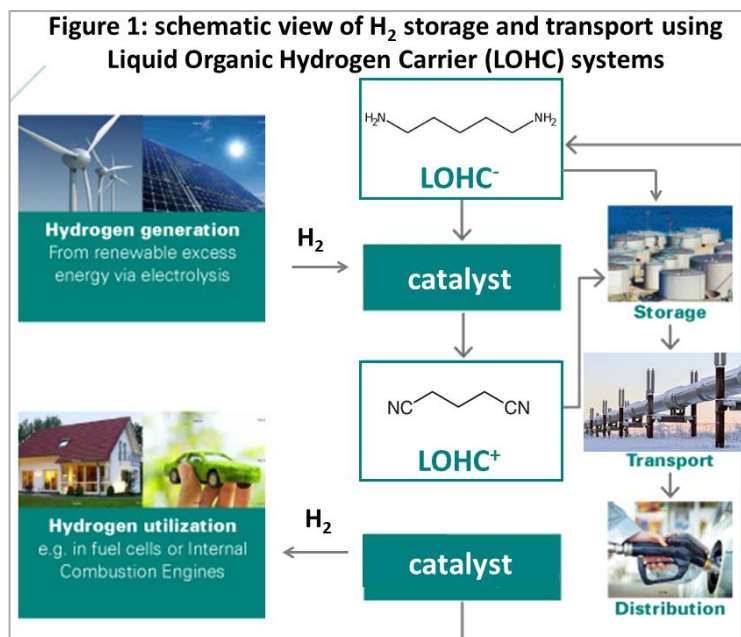
Scientific approach: this proposal has three principal objectives, that will be developed within three closely interconnected tasks:

Task 1: Synthesis of colloidal NPs based on 3d metals

Partner 2 and Partner 3 have already successfully developed **affordable, simple and versatile** protocols for the lab scale synthesis of **highly monodispersed colloidal Co NPs** of various sizes (from 4.5 to 8.5 nm⁵) and shapes (spherical vs nanorod⁴) and using an easily accessible and stable complex of Co (ClCo(PPh₃)₃) as precursor. Moreover, they have shown that these protocols could be implemented for other metals such as Ni⁵ or Fe or alloys of these three metals. Hence, the objective of this task will be to produce a library of metallic NPs (pure or alloys) of various sizes, shapes and composition by adapting existing protocols. **There is no identified risk associated with this task.**

Task 2: immobilization on functionalized silica supports

Based on our experience, and on literature,^{1b} the colloidal nanocrystals will, at least partially, progressively lose their catalytic activity due to agglomeration. To solve this issue and to facilitate



the recovery of the catalysts, a tethering of the colloidal crystals on silane-functionalized, high surface area and high pore size (or non-porous) silicas, will be performed. For the functionalization of the silicas, we will use silane bearing terminal functional groups able to strongly interact with the NCs surface (e.g. a dicarboxylic acid function). This task will also focus on the detailed characterization of the functionalised supports and supported catalysts and on their evolution under reaction conditions (with an attention on possible lixiviation and agglomeration).

Partner 1 has an excellent expertise in the grafting of functional silanes on the surface of silica and on the immobilisation of NPs on these functionalised silica surfaces⁶. The only **risk** we identified for this task is that the development of efficient heterogenized nanocatalysts requires a **careful control of the interaction between the particle and the substrate**: it must be strong enough to **prevent the agglomeration** of the NCs or their release in the solution, while **preserving the initial activity** of unsupported NCs. This fine tuning is however possible by controlling the **density of grafted carboxylic acid functions** on the surface of the silica support and/or by replacing carboxylic acid by other functional groups such as thiols or amines.

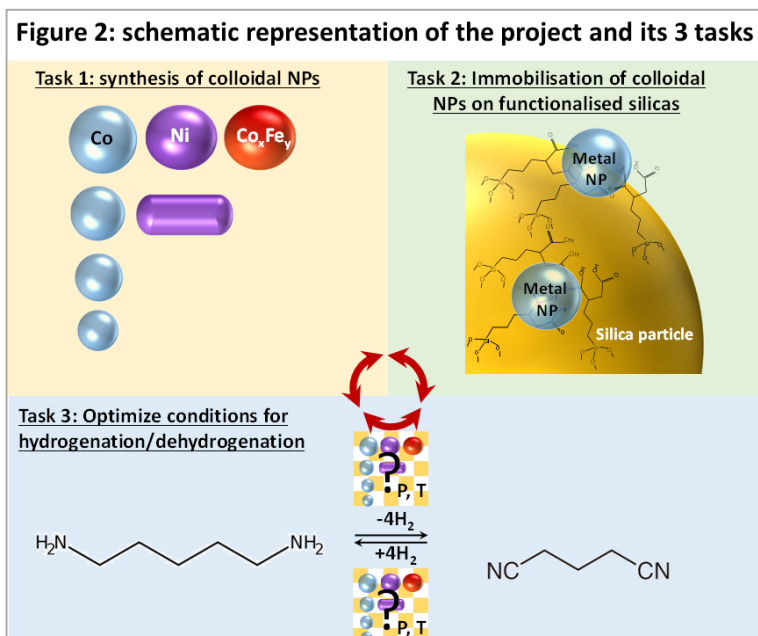
Task3: activity, selectivity, stability & cyclability in dehydrogenation of primary amines/hydrogenation of nitrile

While finding efficient catalysts for the selective and complete hydrogenation of nitrile to amine is relatively easy⁷, the oxidant-free or acceptor-less dehydrogenation of amines to nitriles is still a major challenge as shown by the pioneer works of Szymczak⁸ and Mata⁹ with homogenous and supported ruthenium catalysts. The catalytic activity will therefore first be evaluated for oleylamine dehydrogenation, as partner 2 and 3 have already demonstrated the good activity of the Co NPs for dehydrogenation of oleylamine. Subsequently, 1,5-pentanediamine dehydrogenation and 1,3-dicyanopropane hydrogenation will be explored on the most promising catalysts based on oleylamine dehydrogenation. The 1,5-pentanediamine/1,3-dicyanopropane pair has been chosen because of their physicochemical properties (low toxicity, high boiling point, low melting point) and because they are very interesting in terms of hydrogen gravimetric content (7.9 wt% hydrogen), and a hydrogen volumetric storage density (0.0687 kg of hydrogen.L⁻¹), two values that largely exceed the minimal values of 6 wt% and 0.030 kg.L⁻¹ established by the U.S. Department of Energy (UDE).¹⁰ Moreover, 1,5 pentanediamine can be obtained from biologically available Lysine by biological synthesis.

Both unsupported (colloidal NPs, Task 1) and silica supported NPs (Task 2) will be tested for these reactions and we will evaluate the impact of the properties of the NPs (size, shape & composition) and of the conditions of its immobilization (size of the support particles, size of the pores, choice of the grafted silane and surface density of grafted silane) on the initial activity (TOF), selectivity and on the cyclability (TON), with the purpose to identify the composition and the experimental conditions leading to optimal hydrogenation and dehydrogenation.

The risk we identified for this step is that determination of the best composition and optimal conditions could be time consuming. However, as the reactions produce or release H₂, a rapid screening will be possible.

The three tasks and their interconnexion are schematically depicted on figure 2.



Skills and coherence of team: the team is composed of 3 partners with complementary expertises: **Partner 1 (LRS-SU, J. Blanchard (PI), Researcher at CNRS)** has a well-recognized expertise in the **functionalization of oxides surfaces with silane**, in the **characterization of surfaces** and in the **immobilization of metallic NPs** on these functionalized surfaces. She also has a good expertise in the

evaluation of the catalytic activities. J. Blanchard will **supervise the project** and be more specifically in charge of **Task 2**, but also participate to **Task 3**. Other members of LRS (S. Boujday, XPS and surface functionalization, Y. Millot ²⁹Si SS NMR) will also bring their expertise to the project)

Partner 2 (C. Petit, MONARIS-SU, Prof.) has a well-recognized competence in the synthesis of nanocrystals and their self-organization in 2D and 3D superlattices. His seminal article on the synthesis of silver nanoparticles was cited more than 800 (In situ synthesis of silver nanocluster in AOT reverse micelles, C Petit, P Lixon, MP Pileni, J. Phys. Chem. 1993, 97 (49), 12974). He has a long expertise on cobalt NCs and Co-based nanoalloys synthesis. He demonstrated a great experience on structural and magnetic characterization of the nanomaterials either in isolated state or as superlattices. His research is now mainly devoted to the development of new syntheses to control the shape, size and structure of (bi)metallic nanocrystals. Besides the empirical process, He models the nucleation and growth processes in order to understand the NCs design (shape, composition and size) and their self-assembly process and optimize their application. He will be in charge of Task 1 but also involved in task 2 and 3

Partner 3 (IPCM-SU, M. Petit, Research Director at CNRS) has a worldwide established knowledge in two main themes in the area of **organometallic catalysis**. One focuses on the **activation of E-H bonds (with E = C, Si, B, H...)** followed by the functionalization of unsaturated compounds using cobalt complexes. The other is focused on the **synthesis of nano-objects by organometallic routes** and their applications in catalysis and in the energy field. **The major common concern to these thematic is the design and the development of simple, well-defined, easily accessible catalytic systems, usable without adding additives and more over easily reproducible.** M. Petit will be in charge of **Task 3** but is also involved in **Task 2 and Task 1**.

References

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⁸ Tseng, K.-N. T. et al. *J. Am. Chem. Soc.* **2013**, *135*, 16352; [10.1021/ja409223a](https://doi.org/10.1021/ja409223a)
⁹ Ventura-Espinosa, D.; Marzá-Beltrán, A.; Mata, J. A. *Chem. - Eur. J.* **2016**, *22*, 17758. [10.1002/chem.201603423](https://doi.org/10.1002/chem.201603423)
¹⁰ <https://www.energy.gov/eere/fuelcells/hydrogen-storage>

2 b) Research plan with provisional calendar

The project will benefit from the expertises and the infrastructures of the three involved laboratories. Moreover, as the three labs are located close to each other, the PhD student will be able to organize his/her experimental work easily, on a day-to-day basis and the supervisors will easily communicate with each other. The calendar proposed below is a provisional one that could be easily modified according to the progresses of the project.

1st Semester (Task 1, first part): Synthesis and characterization of a library of Co colloidal NPs of various size and shapes using existing protocols

2^d Semester (Task 2, first part): functionalization of silica surface with silane (e.g. 3-(triethoxysilyl)propylsuccinic anhydride) and immobilisation of Co NPs. Characterization of functionalised surfaces (XPS, ²⁹Si NMR...).

3^d Semester (Task 3, first part): evaluation of catalytic activity and cyclability of supported and unsupported Co^o catalysts (with a focus on the stability of catalysts)

4th Semester (Task 1, second part): synthesis of CoNi and CoFe bimetallic NPs

5th Semester (Tasks 2&3, second part): immobilization of bimetallic NPs on functionalized supports; evaluation of their activity, stability and cyclability.

6th Semester: finalization of the experiments: preparation of the manuscript and of the PhD defense.