

## Controlled immobilization of tailored nano-particles on meso-zeolites for CO<sub>2</sub> conversion to light olefins.

### Immobilisation contrôlée de nanoparticules sur des zéolithes mésoporeuses pour la conversion du CO<sub>2</sub> en oléfines légères.

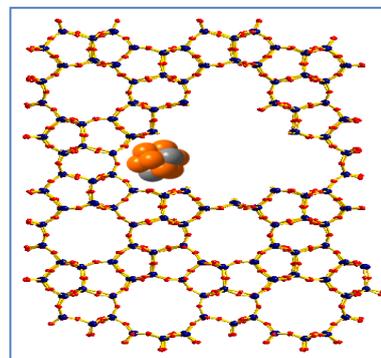
#### General Objectives.

CO<sub>2</sub> emission has been continuously growing. Though CO<sub>2</sub> is the major anthropogenic greenhouse gas, it might serve as a carbon feedstock to produce chemicals and important building blocks. Hence, research efforts in the capture and transformation of CO<sub>2</sub> have become vital.<sup>1</sup> Moreover, the decrease of fossil resources consequently directs the research interests towards the utilization of CO<sub>2</sub> as an alternative carbon source.<sup>2</sup> CO<sub>2</sub> presents advantages such as nontoxicity, abundance, and is regarded as a renewable chemical feedstock. However, the conversion of the stable CO<sub>2</sub> molecule usually requires supplementary energy input (electrochemistry and electrocatalysis)<sup>3</sup> and/or high energy co-reactants such as H<sub>2</sub> and reactive organic compounds (e.g., epoxide).<sup>2</sup> Various reactions for the valorization of CO<sub>2</sub> have been reported in literature. The hydrogenation of CO<sub>2</sub> is a promising route to produce various chemicals such as methanol, formic acid, dimethylether, and light olefins.<sup>4</sup> More important, ethylene and propylene have an even larger industrial application and are now used for the synthesis of numerous products (polymers as PE, PP). The demand of ethylene and propylene is in constant growing from all parts of the world with a 5% rate per year.<sup>5</sup> Different processes have been developed and some of them are currently running. For example, propylene can be obtained by propane dehydrogenation or by ethylene and butenes cross metathesis. In order to reduce the dependence to oil, processes that produce light olefins from alternative resources, *i.e.* coal, natural gas or even biomass, have been developed. An innovative process, namely MTO (Methanol To Olefin) that affords light olefins (*i.e.* ethylene, propylene and butenes) by conversion of methanol on acidic supports (SAPO-34, ZSM-5) has been developed by UOP and Hydro. However, methanol used in the MTO process is originated from fossil sources such as coal and natural gas, *via* syngas (CO/H<sub>2</sub>). Hence, a primary challenge to make this process sustainable is to employ methanol produced from a sustained source, ultimately from CO<sub>2</sub>. With hydrogen available from renewable sources (photocatalytic splitting of water, water electrolysis using solar or wind energy), the production of propylene and ethylene by hydrogenation of CO<sub>2</sub>, which are exothermic reactions, would be highly desirable from the viewpoint of utilizing CO<sub>2</sub> as a carbon feedstock for the production of chemical building blocks. The aim of this project is to develop new heterogeneous catalysts for a single step conversion of CO<sub>2</sub> to ethylene and propylene. It is a sustainable and environmental friendly process using the abundant CO<sub>2</sub> as feedstock. Furthermore, the targeted products (ethylene/propylene) may contribute to meet the increasing propylene demand and equilibrate their supply from by-products and on-propose technologies. The targeted products can be obtained in a single reactor through cascade reactions starting from CO<sub>2</sub> to methanol followed by MTO.

#### Conversion of CO<sub>2</sub> to ethylene and propylene through MTO.

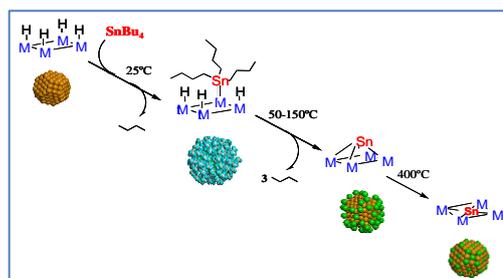
Our approach will be focused on the development of a new class of heterogeneous catalysts including meso-porous zeo-type materials decorated with well-defined bimetallic nanoparticles. To date, the use of such catalysts as catalytic materials for selective reduction of CO<sub>2</sub> to ethylene and propylene is unknown.

\* The meso-porous zeo-type materials constitute a fundamental base of this first part of the project. It is important to control size of the meso-pores (for deposition of the metallic phase) and micro-pores (bearing Brønsted protons) of the support. The micro-pore size is first of all given by the choice of the zeo-type structure and the post-treatment. Product (ethylene and propylene) selectivity is mainly controlled by the dimensions of the window of the cavity where the Brønsted proton is localized. A fairly large cavity is necessary in order to host the organic intermediates (based on methylated aryl fragments), according to the hydrocarbon-pool mechanism.<sup>6</sup> On the other hand, it has been found that small openings are desired (4 Å, 8-membered ring) in order to obtain high selectivities to light olefins. Larger openings (7 Å, 12-membered ring) may result in higher by-product contents, such as aromatics. There are several methods to create meso-pores in zeo-type materials, including post-



treatments (acid, base, steam,  $\text{SiCl}_4$ ) and application of templates during the synthesis followed by calcination.<sup>7,8</sup> We have already published the use of meso-porous H-ZSM5 in surface organometallic chemistry of Ga in order to produce a highly active bifunctional catalyst for propane aromatization.<sup>9</sup> Hence, the first part of this project will be dedicated to the preparation of suitable meso-porous zeo-type materials. Different methods to create meso-pores in the zeo-type materials will be explored. The resulting materials will be characterized by XRD, TEM, BET, solid state NMR, IR and their acidity specified by adsorption of ammonia and pyridine.

\* Previous work in the  $\text{CO}_2$  reduction to methanol has been focused on developing multifunctional catalysts based on Cu together with different modifiers (Zn, Ga, B, Cr, etc.). A simplified mechanism of multistep surface reactions is proposed in the case of  $\text{CuZnO}/\text{Al}_2\text{O}_3$ : i) formation of carbonate species after  $\text{CO}_2$  adsorption on the CuO surface; ii) reduction of the adsorbed formate intermediate species by hydrogen to methanol. The most important parameter associated to the catalytic performance in  $\text{CO}_2$  conversion is to obtain a high dispersion of the Cu active sites on the surface. Indeed, the dispersion is directly linked to the preparation of the catalyst, in which precursors, methods and treatments have a direct influence. Moreover, according to this mechanism, an adjacent Zn center next to the active Cu is necessary.



The grafting of metallic precursors on supports<sup>10</sup> is an established methodology that affords well defined heterogeneous catalysts through the grafting of organometallic species on surface hydroxyls of classical supports and on surface of supported group VIII nanoparticles. We reported recently the formation of highly dispersed copper nanoparticles by reaction of silica supported mesitylcopper species  $\text{Cu}(\text{Mes})/\text{SiO}_2$  (obtained by reaction of the silica surface with  $[\text{Cu}(\text{Mes})]_4$ ) with hydrogen at 350 °C, affording nanoparticles around 2 nm size.<sup>20</sup> Hence, the first step to obtain the supported bimetallic nanoparticles in meso-pores of zeo-type materials involves the grafting of  $\text{Cu}(\text{I})\text{Mesityl}$  on dehydroxylated meso-porous zeo-type materials. The monometallic nanoparticles will then be obtained after reduction with hydrogen at a low temperature. This material will serve as a starting material to obtain the proposed bimetallic catalysts by modification by Sn, Zn and Pd. The second step consists in the grafting of suitable organometallic precursors ( $\text{ZnR}_2$ ,  $\text{SnR}_4$ ,  $\text{PdR}_2$ , R = alkyl, allyl, aryl) onto the previous Cu-nano-particles in meso-porous zeo-type supports.<sup>21</sup> All resulting species will be characterized by chemisorption of  $\text{H}_2$ ,  $\text{O}_2/\text{H}_2$  titration, TEM, IR, elemental analysis, XPS, EXAFS.

\* Catalysts testing and ranking will be performed in a flow continuous reactor, including evaluation of the regenerability and the optimization of the reaction conditions, including effect of the  $\text{H}_2/\text{CO}_2$  ratio by control of the  $\text{H}_2$  concentration to limit deactivation; these tests will be focused on maximizing activity at low temperature ( $\leq 400^\circ\text{C}$ ) and catalyst stability. The exact conditions for tests will be defined in preliminary experiments. Input from the catalytic data should allow analysis of structure/activity relationships and reaction mechanism, also on the basis of theory/modelling, improve catalysts that can be designed. Micro-kinetic modelling of the catalytic reaction should assist the optimal catalyst design and the development of a reactor model which will allow simulating the performances that can be obtained in the integrated system. In-situ and in-operando techniques (IR, XAS, and XRD) will be applied to further gain knowledge on the system, notably with respect to the mechanism. Furthermore, XRD will be applied to determine the crystallinity of the fresh and aged catalysts, giving directly information on its stability.

## References

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