

### 3. Surface chemistry and catalysis

#### Particles with properties triggered by an external stimulus

##### a. Iron carbides

During the last years preceding this report, the group developed the synthesis of NPs that are difficult to prepare by non-organometallic routes, particularly iron and cobalt. Monodisperse iron particles have both magnetic properties and catalytic properties. Thus, the iron NPs are very active in Fischer-Tropsch synthesis and a size effect could be demonstrated both on the activity and the selectivity of the reaction. ([ACS Catalysis 2016](#)). In addition, a proof of concept on the possibility for these particles to heat when subjected to an alternating magnetic field was obtained in 2012. However, the iron particles are extremely sensitive to oxidation, which limits their use. The decomposition of a metal carbonyl under H<sub>2</sub> (Mn, Co, Ru) allows, depending on the conditions, to synthesize a series of NPs of iron and iron carbides of type FeC@Mn, Fe@FeCo, FeC@Co, Fe@FeRu, FeC@Ru ([NanoLett 2015](#)). The formation of carbide is due to the easy penetration of carbon into the iron lattice when CO is reduced. On the basis of these results, we have shown that it is possible to introduce a controlled quantity of carbon and to obtain defined phases simply by subjecting the preformed iron NPs to a pressure of 3 bars of CO at 150 °C in mesitylene. In this way we have succeeded in obtaining the phase Fe<sub>2.2</sub>C in majority, unprecedented in the state of NPs, which has magnetic properties similar to iron in terms of anisotropy and saturation magnetization. For all these particles, we studied their heating properties induced by the presence of an alternating magnetic field. For the particles mainly composed of Fe<sub>2.2</sub>C, heating powers up to 3kW / g were obtained (46 mT, 100 kHz), that is to say, more than one order of magnitude higher than any other material ([Angew Chem 2016](#)). The production of these new phases can be facilitated by the capture of the water produced by the reduction of CO ([ChemCatChem 2018](#)). These NPs of iron carbide are the active phases in Fischer-Tropsch synthesis. However, the involvement of carbide-trapped carbon in the reaction itself is unclear. To study the role of these carbides, we synthesized Fe<sub>2.213</sub>C NPs and demonstrated that "carbide" carbons do not participate in the Fischer-Tropsch reaction thanks to a gas phase NMR study. ([ChemCatChem 2016](#)).

These particles were used in catalysis but we had to face a first problem: the heating power of the particles could, under the same conditions, vary from more than 2kW / g (Fe) to 0 whereas the magnetic properties measured by VSM seemed identical. We have been able to elucidate this problem, particularly through the use of high frequency magnetic measurements and demonstrate that this problem is due to the dipolar couplings that slow down the mobility of particles. The coupling can be controlled by modulating the concentration of ligands on the surface of the NPs leading to perfectly reproducible results ([Nanoscale 2019](#)).

These NPs are able to hydrogenate CO<sub>2</sub> to CH<sub>4</sub> when heated magnetically (Fig. 1). In order to develop a process using magnetic heating, we have built a unique "magnetic catalysis" installation which includes a gas supply regulated by flow meters, a glass or quartz reactor placed inside a coil fed by an inductor and online analysis by GC-MS. The performances of the Fe<sub>2.2</sub>C NPs were modest (3% methane yield, 1 bar CO<sub>2</sub> / 4H<sub>2</sub> mixture). In order to improve them, FeC @ Ni NPs were synthesized which proved to be better (20% yield, under the same conditions). To increase the yield, the FeC NPs were used to heat a catalyst composed of NPs of sizes of about 2 nm of a metal deposited on an oxide. (Ru/Siralox, [Angew Chem 2016](#); Ni/CeO<sub>2</sub>, [Catalysis Sci & Tec 2019](#)).

Under these conditions, a methane yield close to 100% at ambient pressure was attained. A modified version of this result is currently being valorised with the SATT of Toulouse (patent filing, project Methamag for the realization of an industrial pilot of biogas enrichment in the Lauragais) and a certain number of industrials, in particular Téréga who takes an option on the process and GrDF that support it.

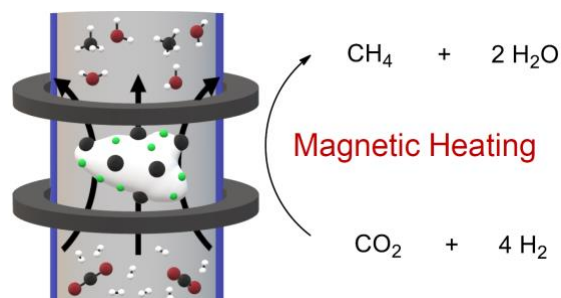


Fig. 1 : Sabatier reaction catalyzed by NPs

The iron carbide NPs are in principle biocompatible. To use them in nanomedicine, they must be rendered soluble and stable in water and have their toxicity tested. This was done in collaboration with the group of V. Rotello (Univ Massachussets). Fe<sub>2.2</sub>C NPs were submitted to ligand exchange using catechol-containing molecules to bind to iron, an alkyl spacer to protect iron, a PEG spacer to expand in water, and a functional group (amine, carboxylic or sulfonic acid). These particles are stable for several months in air and in water. They have the best heating power ever measured in water and depending on the functional groups are biocompatible in vitro. They will be vectorized on specific cell lines ([ACS Nano 2019](#)).

## **b. Bimetallic catalysts**

Iron carbides have exceptional heating power but their reactivity is limited by their Curie temperature which is of the order of 450 ° C. This limit is an advantage for reactions such as the hydrogenation of CO or CO<sub>2</sub> which take place at low temperature (200 to 400 ° C) but prevents the use of these NPs for other reactions of interest such as dry reforming of methane which takes place at 700-800 ° C. For this, we have prepared FeCo and FeNi NPs.

The FeCo particles (T<sub>c</sub> 1000 ° C.) were synthesized according to a process described for Fe<sub>50</sub>Co<sub>50</sub>, but the relative concentration of iron and cobalt was varied, which made it possible to modulate the Curie temperature and the heating power of the particles. Four catalytic reactions that operate at temperatures of increasing range have been studied:

- CO<sub>2</sub> hydrogenation (T = 300-400°C) : excellent yields have been obtained using very weak magnetic fields, which demonstrates the advantage of using materials with a Curie temperature significantly higher than that of the reaction to be performed ;
- Propane dry reforming (T = 500-600°C) : the propane is entirely converted ;
- Methane dry reforming (T = 600-700°C) : a significative conversion has been obtained (15%) ;
- Propane deshydrogenation (T > 700°C) : Yields superior to 10% have been attained. In this case it was also necessary to develop a PtSn / Sialox catalyst by an organometallic chemistry method.
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These examples demonstrate the potential of magnetic heating for difficult catalytic reactions and this study will be continued.

In parallel FeNi<sub>3</sub> NPs were prepared. These particles have a relatively modest heating power but are catalytically active for the hydrogenation of CO<sub>2</sub>. Our goal here was to determine if the concept of a single catalytic heating particle could lead to a convincing result in catalysis. This result was obtained by enriching the surface of the particles with nickel. The FeNi<sub>3</sub>@Ni particles are the only ones to date that can give a 100% methane yield during the hydrogenation of CO<sub>2</sub> and without any other catalyst deposited on the support.

## **c. Heterogeneous catalysis in solution**

The magnetic NPs described above (FeC<sub>x</sub>, FeCo, FeNi<sub>3</sub>) have considerable heating powers that allow to perform reactions at high temperatures. A difficulty of heterogeneous reactions is their heat management, especially for very exothermic reactions. The reactions performed in solution are much better in dealing with this problem but they are limited to relatively mild conditions (<200 ° C).

Since magnetic NPs can be brought to temperatures much higher than the boiling point of the solvent, when used in solution, this should give rise to a vaporization of the solvent in the vicinity of the NP and therefore to a bubble in which the steam would be overheated and at high pressure, similar to the cavitation observed in the presence of ultrasounds. To try to highlight this phenomenon, we are interested in the hydrodeoxygenation of aromatic ketones, a major reaction of biomass conversion, especially concerning furfural and furfuralacetone. Quantitative yields and total selectivities to hydrodeoxygenation products were observed (without reduction of the aromatic cycle). However, it is important to underline that the experimental conditions used (Fischer-Porter bottles and a pressure of 3 bars of H<sub>2</sub> and standard conditions of magnetic induction: 60 mT, 300 kHz) are not comparable to the ones in conventional systems (200 and 300 ° C and 50 bar). This amazing result opens up new possibilities for performing difficult transformations in organic chemistry ([Angew. Chem. Int.Ed. 2019](#)).

## **d. Electrochemistry and catalysis**

The electrolysis of water has a better energy balance at high temperatures. We wanted to determine whether the magnetic heating of NPs with a nickel-rich surface could allow a significant energy gain. For this, we chose the Fe<sub>2.2</sub>C@Ni NPs, previously used in catalysis. These particles have, in the absence of any magnetic heating, excellent properties in electrocatalysis which place them at the same level as the iridium NPs, among the most active catalysts for the most difficult steps, namely water oxidation and oxygen evolution. In addition, we have elaborated a device that can measure the electrocatalytic activity of these NPs in the presence of an alternating magnetic field and after deposition on a carbon felt. A considerable gain of 200 mV was achieved, (Coll. J. Deseure et M. Chatenet du LEPMI à Grenoble, J. Carrey de l'équipe Nanomag, ANR HyWally, [Nature Energy 2018](#)).