# Gas-phase study of the metal-CO₂ interaction for an improved efficiency of catalyzed CO₂ reduction

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Context of the study

In the context of the climate change emergency, the European Union has fixed a carbon neutrality objective to 2050.[1] Among the envisaged strategies, an increase of carbon sinks, either natural or technological, is foreseen. In that case, the chemical utilization of CO_2 appears as a promising way as carbon dioxide may indeed represent one of the primary sources of carbon and can thus be used as a prospective replacement for oil, coal or fuels. In this field, activation of CO_2 is permitted by a first reduction step which is catalyzed using electrochemical or photochemical processes. An increasing number of systems have been developed over the years to improve the efficiency and selectivity of this reduction step,

by varying the metals, control the reaction medium, develop new materials and structures, etc., but there is still a lot of effort to make this strategy become a viable approach for the carbon neutrality objective. This holds particularly true for the fundamental understanding of the multistep CO_2 reduction mechanism, the role played by the metals, ligand and surfaces on the rate determining step of the reaction and the stability and structures of the involved intermediates. All this knowledge would undoubtedly help to the design of more efficient catalysts and therefore lead to improved reaction efficiencies. **To date, the fundamental knowledge on the chemical reactivity of these metal-based compounds is mostly built on diffuse and rare information,[2a, b, c, d, e, f] and besides rare attempts,[3a, b, c, d] no large-scale study exists on the features of the metal-CO₂ interaction depending on the metal or the influence of complex environment on CO₂ on the metal catalytic strength. The main objective of this PhD project is to fill this gap and provide an exhaustive, complete and systematic study on metal activities in the form of molecular trends, representing the key factors as: reaction rates, stability and electronic properties.**
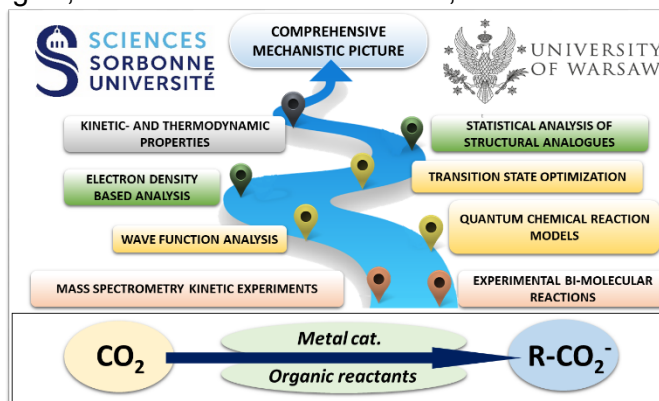
Scientific objectives

The goal of this PhD project is to explore - in a systematic way - the metal-CO₂ interaction along the periodic table in order to provide experimental quantitative knowledge on how metal atoms interact with CO₂ molecule and –CO₂⁻ moieties incorporated within diverse organic structures. Investigation of the chemical interactions between the metal-organic (M-R) compounds and the CO_2 molecules that lead to the formation of appropriate carboxylates will bring a valuable information about the catalytic abilities of the metal atoms in the CO_2-capturing prospective technologies. Furthermore, description of the formation reaction of metal-carboxylate complexes and their fragmentation mechanisms will organize the knowledge about the stability of the CO_2-accumulation molecular architecture. Finally, the description of the kinetic properties of metal-carboxylate and metal-CO₂ reaction will give a useful tool for electrochemical and technological design processes. Taking above, it is intended to recognize and describe the subtle relationships between electronic structures, molecular size and reaction energy requirements of the key moieties within the chemical molecules. In this way, we want join our efforts, share our unique and state-of-art experimental techniques and theoretical experience to **obtain key insights into the physical factors across molecular systems that govern CO₂ reduction catalyzed by metal atoms at the most fundamental level.**

Scientific approach

Both partners involved in the project has developed a long-time expertise in **experimental gas-phase chemistry**, in particular in the measurement of **thermochemical quantities** on the French side[4a, b, c] and in **ion-molecule reactions** on the Polish one.[3a, 5] Gas-phase studies are particularly relevant in the context of this project because most of the CO_2 reduction reactions occur - at least

partly - in the gas phase and this phase is also the most suited to evaluate intrinsic properties of molecules. The most appropriate dedicated tool in this context is mass spectrometry as it is known to be one of the rare experimental techniques able to provide either accurate thermochemical data[6] or to give access to a fine elucidation of reaction mechanisms through the identification of elusive and "*short-living*" intermediates.[7a, b]

Taking advantage of the complementary profiles and skills of the two supervision teams, the PhD candidate will have access to state-to-the-art instruments in Paris and Warsaw to:

(i) Provide for the first time a complete description of the metal-CO_2 reactivity, including the effect of the metal along the periodic table, using a designed state-of-the-art instrument implemented in Warsaw University.

This extensive study will provide an extensive overview of the RCO_2 reactivity towards a large range of metals in order to rationalize the differences that are observed in CO_2 reduction reactions by means of efficiency or selectivity, depending on the metal catalyst used and organic ligand size.

(ii) Quantify the interaction between the metal and the CO_2 moiety using a methodology developed within the Sorbonne University group which includes mass-spectrometry based experiments and kinetic modelling.

The French team has developed a strong expertise in the MS-based measurements of thermochemical quantities of ion dissociation in the gas phase for several years now. This includes the use of well-documented threshold-CID[8a, b] or BIRD[4b] methods but also the development of new approaches such as the use of multi-collisional regime[4a, c, 9] or of low-energy CID in a linear ion trap,[10] both providing high accuracy results. The PhD candidate will thus have access to various mass spectrometers and approaches to evaluate the metal-CO_2 bond strength with the highest accuracy.

(iii) Support experimental results through an extensive theoretical work, involving bond-dissociation energy calculations and electronic structure calculations of the reaction mechanism.

The PhD candidate will be trained to state-of-the-art quantum chemistry modelization in order to support the experimental results by calculating reaction rates, equilibrium and transition state structures as well as bond-dissociation energies (BDEs). This theoretical study will help to benchmark theoretical methods which will be useful as predictive tools for new catalytic systems.

Link to the 4EU+ Flagship #4 "Environmental transition"

This PhD project clearly falls within the "*Environmental transitions*" flagship as it aims at getting a deeper understanding of one of the most promising strategies to reach carbon neutrality. From the fundamental knowledge that will be acquired with this PhD project at the molecular level, a better rationalization of the catalyst design will be possible and will lead to more efficient systems and materials to envisage the CO_2 chemical utilization as viable or even main carbon sink.

Profile of the PhD candidate:

Master degree in Physical Chemistry, Chemical Physics or Chemistry; Very good communication and writing skills; First experience in mass spectrometry will be positively considered.

References

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