PhD thesis: Ultradispersed rhenium-based catalysts for the selective hydrogenation of carbon dioxide

Context: The development of efficient and inexpensive catalysts for the production of chemical energy-carrying molecules is an important current challenge, and CO_2 hydrogenation to alcohols – mostly methanol and ethanol – is a strategy of choice.[1] Through this process, while reducing anthropogenic CO_2 emissions, valuable energy carriers (fuels) and platform-molecules (for chemical synthesis) can be generated. Regarding the catalytic materials, a recent and promising approach is to maximize the utilization of metals by atomically dispersing them onto high-surface-area supports. The resulting "single-atom catalysts" can exhibit improved performances with respect to conventional supported nanoparticles.[2]

Objectives: In this thesis project, we wish to design cost-effective catalysts based on early transition metals atomically dispersed over transition metal oxides (examples of electron microscopy images in Figure 1a,b) for the selective hydrogenation of CO_2. We have already obtained remarkable results for molybdenum ultradispersed on rutile titania for methanol synthesis.[3,4] Preliminary experiments have revealed the even higher potential of oxide-supported rhenium, a non-critical metal, for orienting the CO_2 hydrogenation reaction toward methanol, methane, or higher alcohols/hydrocarbons. As a matter of fact, the selectivity appears strongly sensitive to the nature of the oxide phase, as illustrated in Figure 1c. An important objective of the thesis will be to understand this effect as well as the influences of the metal loading/dispersion and the oxide surface modifications (oxygen vacancies, promotors…) in order to design catalysts with maximum alcohol selectivity while keeping high activity and stability.

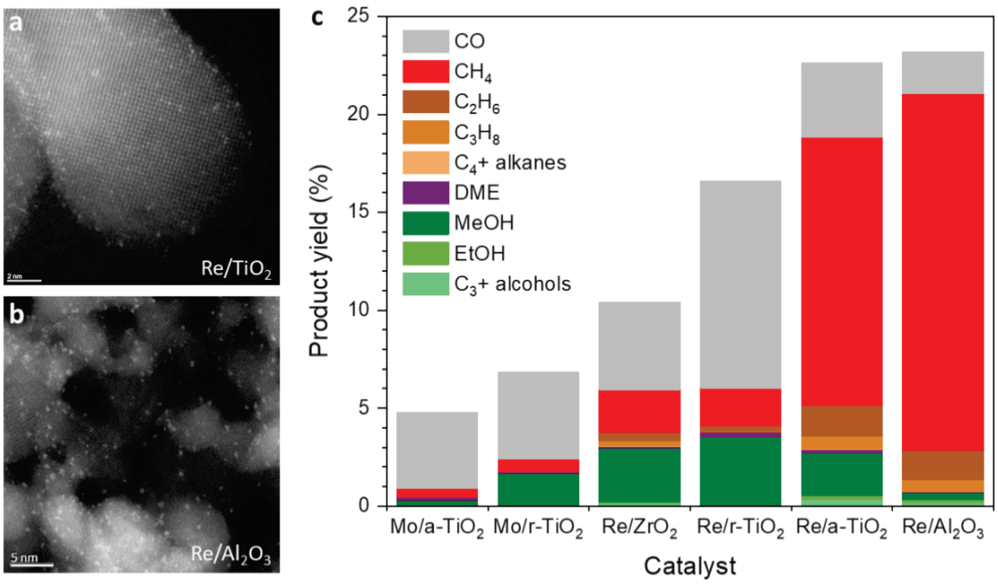

Figure 1: a,b) STEM-HAADF images showing single atoms and few-atom clusters of rhenium (white dots) on anatase titania (a) and gamma alumina (b). c) Comparison of oxide-supported Mo and Re catalysts (same molar loadings) for CO_2+H_2 (1:3) reaction at 3 MPa and 275 °C.

Methodology: The PhD thesis will involve in-depth investigations of Re/oxide catalysts to rationalize these observations and thereby steer the catalyst design towards more active and selective materials. Chemical preparation methods combined with structural characterization and catalytic testing in a dedicated high-pressure flow reactor will be employed. IRCELYON is equipped with state-of-the-art techniques, such as environmental aberration-corrected transmission electron microscopy (ETEM) and *operando* diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) associated with steady-state isotopic transient kinetic analysis (SSITKA), which will be used throughout the work to gain insight into the catalyst behavior.

(1) De, S.; Dokania, A.; Ramirez, A.; Gascon, J. Advances in the Design of Heterogeneous Catalysts and Thermocatalytic Processes for CO2 Utilization. *ACS Catal.* **2020**, *10* (23), 14147–14185. https://doi.org/10.1021/acscatal.0c04273.

(2) Wang, A.; Li, J.; Zhang, T. Heterogeneous Single-Atom Catalysis. *Nat. Rev. Chem.* **2018**, *2* (6), 65–81. https://doi.org/10.1038/s41570-018-0010-1.

(3) Len, T.; Bahri, M.; Ersen, O.; Lefkir, Y.; Cardenas, L.; Villar-Garcia, I. J.; Dieste, V. P.; Llorca, J.; Perret, N.; Checa, R.; Puzenat, E.; Afanasiev, P.; Morfin, F.; Piccolo, L. Ultradispersed Mo/TiO2 Catalysts for CO2 Hydrogenation to Methanol. *Green Chem.* **2021**, *23* (18), 7259–7268. https://doi.org/10.1039/D1GC01761F.

(4) Len, T.; Afanasiev, P.; Yan, Y.; Aouine, M.; Morfin, F.; Piccolo, L. Operando X-Ray Absorption Spectroscopic Study of Ultradispersed Mo/TiO2 CO2-Hydrogenation Catalysts: Why Does Rutile Promote Methanol Synthesis? *ACS Catal.* **2023**, 13982–13993. https://doi.org/10.1021/acscatal.3c02149.

Required profile: Master degree in physical chemistry, materials chemistry, heterogeneous catalysis, or equivalent. Any preliminary know-how in catalysis lab experimentation and analytical measurements is desirable.

Our group: The CO_2 hydrogenation group at IRCELYON currently involves a CNRS researcher, a CNRS research engineer, a post-doc, two PhD students, and a Master student. We are experts in heterogeneous catalysis and materials science. We use advanced structural characterization techniques (ultrahigh-resolution electron microscopies, operando spectroscopies, synchrotron X-ray techniques…) to unravel reaction mechanisms and develop novel catalytic materials.

Contact: Send a CV and a cover letter to Dr. Laurent Piccolo (laurent.piccolo@ircelyon.univ-lyon1.fr) and Dr. Franck Morfin (franck.morfin@ircelyon.univ-lyon1.fr).

Why coming to IRCELYON:

- The largest research institute of heterogeneous catalysis in France
- Stimulating working environment, with students from all over the World
- Neighboring corporate restaurant proposing lunch at low cost
- Easy access by public transport + private car park
- Partial refund of transportation tickets + sustainable mobility bundle
- Financial participation in mutual insurance costs