



PhD Proposal 2017

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| Title: Controllable synthesis of Fe/CNTs based catalysts for CO₂ hydrogenation |
| Scientific field: Heterogeneous catalysis |
| Key words: carbon dioxides, Iron-based catalyst, hydrogenation, particle size |

Details of the subject

Background, Context

Nowadays, the fossil feedstocks such as coal, oil and natural gas are essential for the production of energy and commodity chemicals. The consumption of fossil feedstocks leads however, to major CO₂ emission. CO₂ is considered as one of the most abundant greenhouse gases, enhancing the “greenhouse effect” and further influencing the climate changes. Therefore, CO₂ capture and utilization (CCU) attract more and more interests^[1].

CO₂ hydrogenation offers the opportunity to produce a wide range of fuels and chemicals. The type of products obtained is strongly dependent on the type of catalysts^[2]. One of promising processes is CO₂ hydrogenation for the production of alcohols and unsaturated hydrocarbons^[3]. In this context, Fe-based catalysts have received widely attention due to the low cost and highly olefinic nature of the products. Different reaction mechanisms are discussed in the literature. Some of them suggest that the reaction proceeds via intermediate formation of carbon monoxide by reverse water gas shift (RWGS) reaction. The resulting CO then undergoes dissociation and carbon chain growth to generate oxygenates and hydrocarbons by Fischer-Tropsch reaction^[4]. Other mechanisms involve direct hydrogenation of carbon dioxide to the target compounds (e.g. methanol and other oxygenates). A clear understanding of the reaction mechanisms is therefore a major challenge of carbon dioxide hydrogenation.

Carbon nanotubes (CNTs) have well-defined hollow interiors and exhibit unusual mechanical and thermal stability as well as electron conductivity. They can also be considered as modelled catalysts for understanding the effects of nanoparticle confinement in a number of catalytic reactions^[5, 6]. The catalytic performance of carbon nanotubes is strongly affected by location of metal nanoparticles either inside or outside of the nanotubes. Bao *et al.* [*W. Chen, Z.L. Fan, X.L. Pan, X.H. Bao, J. Am. Chem. Soc. 130 (2008) 9414-9419*] observed that when the metal particles are located inside the nanotubes, a micro-environment with higher concentration of active hydrogen species is formed and the reaction rate in Fischer-Tropsch synthesis is significantly enhanced. Such a feature may make the catalyst to have exceptional performances in CO₂ hydrogenation^[7].

Therefore, a clear understanding of the reaction mechanism and influence of metal nanoparticle confinement represent major challenges in CO₂ hydrogenation. The key challenge lies here in the preparation of the catalysts with homogeneous dispersion of iron oxides either inside or outside of the CNTs (Figure 1), precise control in particle size –product distributions and catalyst transient behavior.

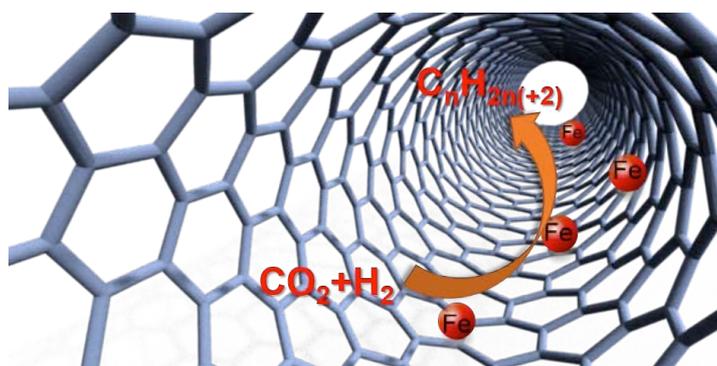


Figure 1 Schematic CO₂ hydrogenation reaction inside CNTs

Research subject, work plan

The present subject aims at understanding the mechanism of carbon dioxide hydrogenation, to develop novel Fe/CNTs based catalytic system, inducing the active phases inside and outside of the CNTs and to study the confinement effect on particle size and product distribution.

The catalyst preparation and optimization of reaction conditions would be carried out at REALCAT high-throughput platform (1st year) in Lille, France. The preparation strategy would involve the conventional impregnation method, but the auxiliary technique including ultrasonic treatment, chemical grafting *etc.* may be used to drive the active phases disperse in CNTs. The method of particle size control is an important parameter, which is directly related to the confinement effect of CNTs. The various techniques would be applied to characterize the acidity/basicity, particle size distribution, dispersion of active phase and metal-support interaction. *In situ* measurements such as XPS, XRD, FT-IR and transient kinetic experiments would be performed to identify the structure, reactivity and localisation of active sites and rates of elementary reaction steps. Correlating the physical-chemical properties with the catalyst performances will provide tools for the control of the product distribution, particle sizes and evolution of active phases during the reaction *etc.* (2nd year).

As an efficient method to improve the reducibility and dispersion of metallic catalysts, the post treatment by glow-discharge plasma would be introduced into the sample preparation process^[8]. This work would be done at Sichuan University, China. In addition, the catalytic stability tests over the best sample would also be also performed during the 3rd year.

This thesis concerns a challenging subject related to reducing global warming and efficient CO₂ utilisation. At the same time it will offer PhD student training in several aspects of process design including: fundamental solid state and catalysis chemistry, in-depth characterization, development of original composite systems, surface chemistry and reaction mechanisms and kinetics.

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