Selective Ethylene production from methanol and syngas mixture

Level: PhD application for the doctoral school program 2026

Profile of the candidate: Master degree in materials chemistry, physical chemistry, heterogeneous catalysis, analytical chemistry, or equivalent. A preliminary know-how in catalysis lab experimentation and analytical measurements is desirable.

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Scientific context: Driving the rapid transition from excessive carbon emission towards a carbon-neutral economy requires adopting multiple strategies for manufacturing more durable chemicals.[1] Next to plastic recyclability, the CO_2-based and biomass-based derivatives including light alcohols, such as methanol, stand as very promising sustainable feedstocks that can significantly reduce the carbon footprint of the chemical industrial processes, especially in the production of light olefins.[2] Ethylene (C_2H_4) is the most demanded building block globally and its production still strongly depends on fossil fuel feedstocks. However, the rising environmental consequences are rending the usage of renewable carbon sources and feedstocks more essential than ever. Herein, methanol, which can be obtained from CO_2 and biomass sources, stands as a very promising sustainable feedstock for a durable C_2H_4 production.
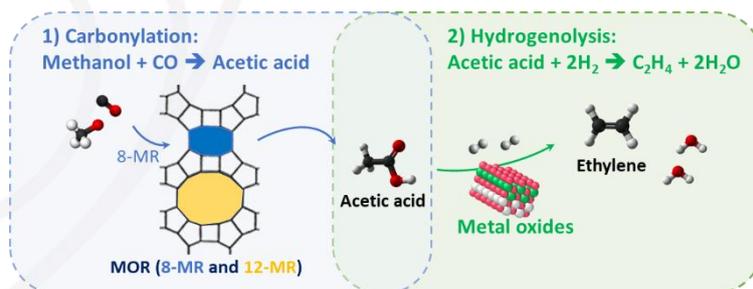

Figure 1: An illustration of the ZeOx process showing the (1) carbonylation of methanol in syngas to acetic acid using mordenite zeolite catalyst and the hydrogenolysis of acetic acid to ethylene on metal oxides.

The most common method for methanol conversion into C_2H_4 is methanol-to-olefins. However, this method shows a relatively low stability and a limited selectivity to C_2H_4, where values in the range of 40 to 60% are often obtained. Recently, the tandem carbonylation and hydrogenolysis of methanol, via the acetic acid intermediate (Figure 1), has been reported showing high C_2H_4 selectivity in the range of 80% combining $ZnO-TiO_2$ and MOR catalysts.[3] Interestingly, this one-step

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process can still benefit from exploring different zeolite-oxide (ZeOx) catalytic systems in bifunctional fashion.[4] In addition, it is essential to deliver a better understanding of the proximity level and its effect on reactivity and selectivity, as well as to optimize the reaction conditions to enhance the catalyst stability.

Missions: In this project, we aim, in a first step, to develop new metal oxide catalysts and test them in the hydrogenolysis reaction of acetic acid. The products identification using analytical tools and the characterization of the key surface properties of the oxide catalysts will consist a considerable part of this project. The most promising oxides will be further tested with a series of tuned benchmark zeolites in the tandem methanol carbonylation and hydrogenolysis.**[6]** Finally, the effect of the proximity between the two catalysts will be explored (bed configuration vs. bifunctional catalysts). Overall, the research questions that we tackle in this project can be summarized as:

- Understand the role of oxygen vacancies in the adsorption of acetic acid and its activation and how acidity is generated on the metal oxide to further dehydrate ethanol into C_2H_4.
- Determine the appropriate hydrogenation potential (desired vs. excessive) required to perform the hydrogenolysis but prevent the hydrogenation of C_2H_4.
- Identify the products pool and characterize the prepared materials in order to establish structure-reactivity relationships.
- Comprehend the role of the water-gas-shift reaction and its effect on the poisoning of MOR zeolite, especially in the systems showing high proximity between the zeolite and oxide functionalities.

For the carbonylation of methanol in syngas-like mixture, a series of tuned MOR zeolites will be used due the remarkable activity of the MOR topology in methanol and DME carbonylation reactions.[5,6] The reaction will be performed in high-pressure gas-phase reactors and the products will be analyzed using a gas-chromatography. Different catalyst loading configurations will be tested in order to study the effect of the proximity between the two catalysts, but also a closer proximity will be aimed by varying the preparation methods (e.g., impregnation and co-synthesis methods). A screening of the reaction conditions will be performed in order to access kinetic and thermodynamic parameters. Finally, the structure properties of the prepared catalysts will be assessed with standard and advanced characterization tools available at IRCELYON (e.g., XRD, TPR/TPD, FT-IR spectroscopy, …).

Bibliography :

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