CO₂ valorization by chemical storage of renewable energy in "decarbonated" methanol and dimethyl ether

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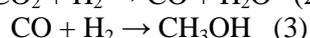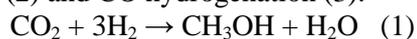[c] *ICS (UPR22-CNRS), 23 rue du Loess BP 84047 67034 Strasbourg Cedex 2, FRANCE*
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More than ¾ of greenhouse gas (GHG) emissions, and mainly CO_2, are due to the energy production by the combustion of fossil fuels. The challenge of sustainable development is the reduction of GHG emissions and the greater penetration of renewable energies into the electricity grid. Valorization of the captured CO_2 coupled with H_2 production by water electrolysis with renewable energies makes it possible to produce "decarbonated" chemical intermediates of high added values (CH_4, CH_3OH or DME). The synthesis of CH_3OH from CO_2 is a very attracting way; it allows producing a liquid energy vector easily storable and transportable. Direct DME synthesis from CO_2 would be even more economical and beneficial as it seems to be a superior candidate for high-quality diesel fuel in near future.

The aim of our project is firstly to develop selective **catalytic materials for the CO₂ hydrogenation** into methanol and secondly to use composite catalytic materials adding an acidic function (zeolite or Al-TUD-1) for the **direct DME synthesis from CO₂**. Several reactions can occur during CO_2 methanolation: CO_2 hydrogenation (1), reverse water gas shift (2) and CO hydrogenation (3).

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad (1)$$
$$CO_2 + H_2 \rightarrow CO + H_2O \quad (2)$$
$$CO + H_2 \rightarrow CH_3OH \quad (3)$$
$$2CO_2 + 6H_2 \rightarrow CH_3OCH_3 + 3H_2O \quad (4)$$

In this work, we propose catalytic materials based on CuO, ZnO, ZrO_2 (CZZ) for the CO_2 hydrogenation into methanol prepared by a continuous microfluidic coprecipitation method where the precipitation zone is much smaller and all parameters are better controlled, thus improving the homogeneity [1]. Parameters influencing the physico-chemical properties, relations between the three components (including 3D-HRTEM) of these materials as well as the catalytic performances were studied (Table 1).

Table 1. Results of catalytic hydrogenation of CO_2 to methanol.

Catalyst	H₂ conv. (%)	CO₂ conv.(%)	CH₃OH sel.(%)	CH₃OH prod. (g·kg_cat⁻¹·h⁻¹)
Industrial [a]	9,1	15,9	53	429
CZZ1 [b] (μ&o)	7,9	17,9	42	871
CZZ2 [c] (μ&w)	8,8	16,4	47	992

Conditions: fixed-bed reactor, H_2/CO_2 = 3.9, 240 - 300 °C, 50 bars, GHSV 25000 h⁻¹ (STP) [2,3]
[a] *similar composition;* [b] *microfluidic synthesis using oil as vector fluid;* [c] *microfluidic synthesis using water as vector fluid*

The catalyst CZZ2 shows the best productivity, due to a better homogeneity and "flower-like" morphology which is certainly more adapted and allows obtaining greater specific surface areas.

This CZZ2 catalyst was used further in the composite mixture with zeolites or with Al-TUD-1 materials for performing the direct DME synthesis from CO_2 (eq.4). Catalytic tests results, discussion of the materials properties as well as the development of methods for *Cu metallic surface area measurements* on Micromeritics AutoChem II and for *acidity measurements by conductometry* (comparison with NH_3-TPD and H^+/D^+) will be discussed.

References

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