

# Storage element – catalyst interaction on different supports for cyclic CO<sub>2</sub> capture and methanation

Giuseppe NAVA<sup>1</sup>, Alessandro PORTA<sup>1</sup>, Roberto MATARRESE<sup>1</sup>, Carlo Giorgio VISCONTI<sup>1</sup>, Luca LIETTI<sup>1\*</sup> <sup>1</sup>Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano – Via La Masa 34, 20156 Milan, Italy \* luca.lietti@polimi.it

#### Significance and Relevance

Dual Functioning Materials (DFMs) for integrated  $CO_2$  capture and methanation are a promising technology for the recycling of  $CO_2$  utilizing green  $H_2$  (Power-to-SNG). In this work, we prepare and compare different DMFs, highlighting synergistic (or detrimental) interaction between the storage element and hydrogenation metal over different supports.

*Preferred and 2<sup>nd</sup> choice for the topic: CO<sub>2</sub> utilization and recycling Preferred presentation*: Oral preferred

## **Introduction and Motivations**

 $CO_2$  plays a central role in the energy transition: different catalytic processes for its hydrogenation into valuable products are gaining momentum, including production of methane, methanol or sustainable aviation fuels (SAF). The catalytic conversion of  $CO_2$  requires a concentrated  $CO_2$  feed, which can be obtained by capturing  $CO_2$  from air or point sources using a liquid or solid sorbent. However, the regeneration of the sorbent is energy intensive, and the separated  $CO_2$  must be typically stored and transported to a conversion facility. Dual Function Materials (DFMs) have been proposed to increase the efficiency of the  $CO_2$  capture and conversion process: by coupling a storage element with a hydrogenation catalyst it is possible to cyclically capture  $CO_2$  from air or flue gases and reduce it to valuable products upon renewable H<sub>2</sub> exposure. For flue gases applications, where  $CO_2$  is available at near atmospheric pressures and temperatures ranging from 150 - 350°C, CH<sub>4</sub> is the preferred target.

Coupling the storage element and the catalytic one over the same support is not necessary, but when using  $Al_2O_3$  as a support a synergistic effect was observed<sup>2</sup>, leading to increased  $CH_4$  formation. In this work we prepare and compare different capture and methanation materials obtained by supporting the storage and catalytic elements on the same support particle, or by physically mixing two different materials.

## **Materials and Methods**

DFMs are prepared through Incipient Wetness Impregnation starting from a commercial  $TiO_2$  (Norpro).  $AI_2O_3$  (Sasol) or SiO<sub>2</sub> (BASF). Sodium Carbonate (Alfa Aesar) or Barium Acetate (Sigma Aldrich) are used as storage element. This and/or Ru nitrosyl nitrate (Alfa Aesar, 32%) are impregnated over the support, dried and calcined at 500 °C. The materials are characterized by BET, XRD, SEM-EDS,  $H_2$  chemisorption, CO<sub>2</sub> adsorption followed by TPD or  $H_2$ -TPSR.

The performance of different materials is assessed by comparing the activity of the mechanical mixture (e.g. Na/TiO<sub>2</sub> + Ru/TiO<sub>2</sub>) with that of the DFM (e.g. Ru/Na/TiO<sub>2</sub>), keeping constant the amount of storage and catalytic element within the microreactor. The materials are tested under cyclic conditions, comprehensive of a capture phase (1% CO<sub>2</sub>, 5 min), a purge phase (He, 5 min) and a methanation phase (4% H<sub>2</sub>, 5 min) at different temperatures (250-350 °C). Gas phase is monitored using a mass spectrometer, an FT-IR analyzer and a micro-GC. The same methodology is used for testing under simulated flue gas conditions, adding 3% O<sub>2</sub> and 2% H<sub>2</sub>O during the adsorption phase. A final heating in presence of H<sub>2</sub> is performed at the end of each experiment to quantify the unreacted adsorbed CO<sub>2</sub>. Selected experiments are replicated in an *operando* FT-IR set-up to obtain mechanistic information.



## **Results and Discussion**

Preliminary results over bimetallic Ru-Na/TiO<sub>2</sub> cycled at 350°C provide a fast methane production in correspondence of the first seconds of the isothermal methanation phase. However, residual CO<sub>2</sub> remains adsorbed on the catalyst surface at the end of the hydrogenation phase. Interestingly, when the mechanical mixture of Ru/TiO<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub>/TiO<sub>2</sub> is tested in the same experimental condition, CH<sub>4</sub> production during the isothermal cycle is significantly higher by 3 times with respect to what observed in the case of the bimetallic Ru-Na/TiO<sub>2</sub>, due to a CO<sub>2</sub> storage capacity at 350 °C which is nearly 3 times higher that that measured using the bimetallic Ru-Na/TiO<sub>2</sub>. This indicates a detrimental effect of the vicinity of the storage and catalytic metal, which is not observed for Al<sub>2</sub>O<sub>3</sub>-supported catalysts<sup>2</sup>, for which a synergistic effect is observed between the CO<sub>2</sub> storage capacity and the methanation activity. Additional catalytic tests and operando characterization is currently ongoing to provide mechanistic explanation for this behavior.

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