

# CO<sub>2</sub> and H<sub>2</sub>O adsorption-desorption cycles for multifunctional Ni-Fe based catalysts in the production of Synthetic Natural Gas

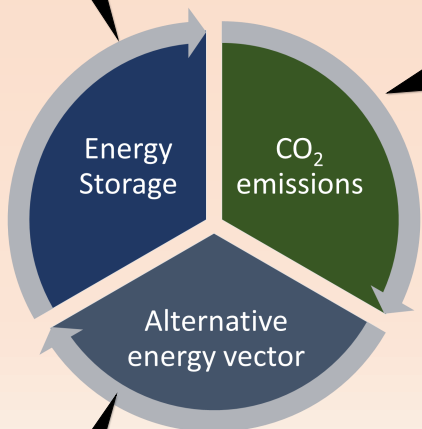
V.D. Mercader, A. Sanz-Martínez, P. Durán, E. Francés, J. Herguido, J.A. Peña

Grupo de Catálisis, Separaciones Moleculares e Ingeniería de Reactores (CREG), Instituto de Investigación en Ingeniería de Aragón (I3A), 50018, Zaragoza, España email: vmercader@unizar.es

## Power to Gas: key role in the energy transition

### ENERGY CHALLENGE

Power to Gas (PtG) technologies have the potential to generate an alternative vector able to cover the energy intermittency of renewables [1]. The surplus electricity from renewables could be used to generate green hydrogen from water electrolysis [1]. That green hydrogen would be combined with a concentrated CO<sub>2</sub> flow, producing high concentrate methane through Sabatier reaction.



The CO<sub>2</sub> captured by (r.1) can have different sources such as industrial CO<sub>2</sub> process emissions or sweetened biogas (70 % CH<sub>4</sub> / 30 % CO<sub>2</sub>). Transforming the CO<sub>2</sub> contained in the biogas into methane, the CO<sub>2</sub> cycle can be closed. Eventually, this technology could have an important role into achieving carbon neutral emissions in energy production.

Upgraded biogas (also called synthetic natural gas) would have a concentration of methane close to 100%, fulfilling the requirements to inject it directly into the preexisting natural gas network. Thus, PtG technologies might produce an alternative energy vector easy to store and transport., whereas H<sub>2</sub> storage and transportation is a challenge with the current technology limitations.

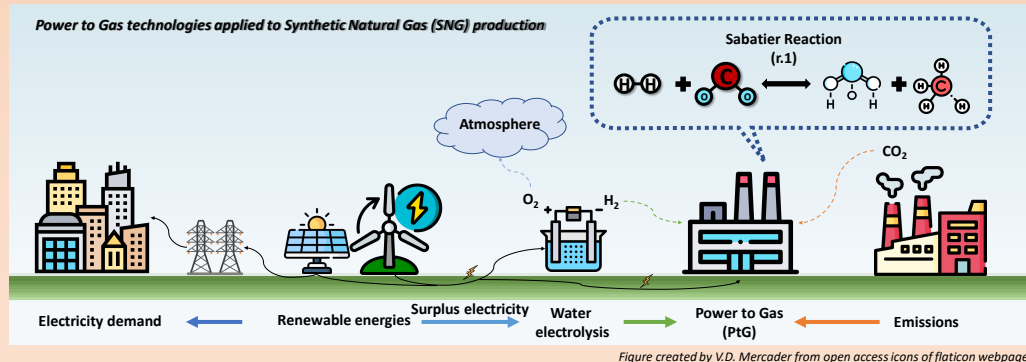


Figure created by V.D. Mercader from open access icons of flaticon webpage

### PtG catalysts intensification

The inclusion of an alkali or an alkaline earth in a nickel-based catalyst could improve the CO<sub>2</sub> affinity of the catalyst, creating chemical bonds between the basic groups and CO<sub>2</sub> [2]. As result, the interaction between the fixed CO<sub>2</sub> with H<sub>2</sub> could be improved. Thus, the selectivity and conversion to methane might increase. In order to study the previously mentioned assumptions, three nickel-based catalysts supported on gamma alumina were synthesized including an alkali or alkaline earth in their composition.

### Experimental

The multifunctional catalysts were synthesized by incipient wetness impregnation from their nitrate or carbonate metallic precursors. In addition, a commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (200 m<sup>2</sup>/g, Puralox, SASOL) was selected as support material for the catalysts. A STA 449 F3 Jupiter (Netzsch) was used for the experiments. The objective of the adsorption-desorption cycles is to spot the interaction of different gaseous species in the adsorption on the catalyst.

#### SAMPLES PRETREATMENTS

The pretreatments included the following steps:  
1. **Preconditioning:** the catalysts were heated at 500 °C in inert atmosphere for 1h.  
2. **Activation** of the catalyst with a 50% flow of H<sub>2</sub> for 1 hour.  
3. **Decreasing the temperature** until 400 °C and **keeping it constant** for 1 hour in inert atmosphere.

Table 1. TGA analysis conditions

Catalyst load	20.0 ± 0.1 mg
Total volumetric flow	100 mL (STP) / min
CO <sub>2</sub> concentration (inlet flow)	40 %
H <sub>2</sub> O concentration (inlet flow)	10 %
H <sub>2</sub> concentration (activation)	50 %
Inert gas (dilutant)	N <sub>2</sub>
Pressure	1 bar
Adsorption steps duration	30 min (each)

### References

- THEMA, M., BAUER, F., STERNER, M. Power-to-Gas: Electrolysis and methanation status review. *Renewable and Sustainable Energy Reviews*. 112 (2019) 775–787. Available from: doi.org/10.1016/j.rser.2019.06.030.
- SABATIER, P., and SENDERENS, J.B. New Synthesis of Methane. *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*. 1902, 134, 514-516. Available from: doi:10.1039/CA9028200333.
- ALTFELD, K., PINCHBECK, D. Reprint: gas for energy 03/2013: Admissible hydrogen concentrations in natural gas systems. ISSN 2192-158X. Available from: https://gerg.eu/g21/wp-content/uploads/2019/10/HIPS\_Final-Report.pdf
- BERMEJO-LÓPEZ, A., PEREDA-AYO, B., GONZÁLEZ-MARCOS, J.A. and GONZÁLEZ-VELASCO, Juan R., 2021. Alternate cycles of CO<sub>2</sub> storage and in situ hydrogenation to CH<sub>4</sub> on Ni-Ni<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>: influence of promoter addition and calcination temperature. *Sustainable Energy and Fuels*. 2021. Vol. 5, no. 4, pp. 1194–1210. DOI:10.1039/d0se01677b.
- RINCÓN, M., MERCADER, V.D., SANZ-MARTÍNEZ, A., DURÁN, P., FRANCÉS, E., HERGUIDO, J., PEÑA, J.A. CO<sub>2</sub> methanation in a Ni-Fe based catalyst fixed bed reactor enhanced by selective water adsorption with LTA zeolites (Sorption Enhanced Sabatier Reaction – SESaR). *Revista "Jornada de Jóvenes Investigadores del I3A"*, vol. 9 (2021), ISSN 2341-4790.

### Acknowledgements

This work has been carried with financing of the project PID2019-104866RB-I00 by MCINN/AEI/10.13039/501100011033.

CREG research group (T43-20R) has been financed by Gobierno de Aragón (Aragón, SPAIN) through FEDER.

Also V.D. Mercader express his gratitude for the grant PRE2020-095679

### Results and Discussion

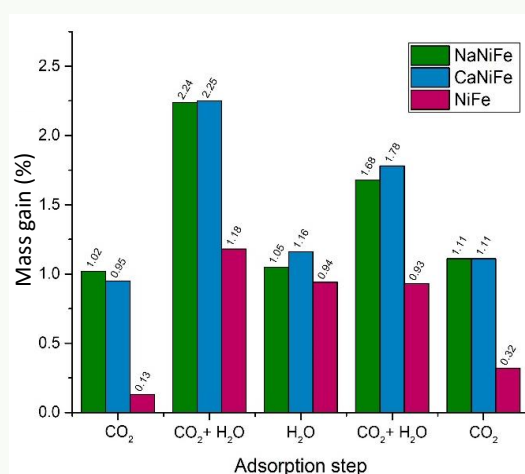


Figure 1. TGA mass gain for catalyst samples subjected to different atmospheres.

### MAIN CONCLUSIONS

The inclusion of alkali and alkaline earth species significantly improved the CO<sub>2</sub> adsorption capacity of multifunctional catalysts. CO<sub>2</sub> was totally removed in step 3<sup>rd</sup> as effect of temperature (400 °C). Water and CO<sub>2</sub> partially compete for the adsorption sites of the catalysts, as it can be observed in the reduction of the mass gain in the 4<sup>th</sup> step in comparison with the 2<sup>nd</sup> one. H<sub>2</sub>O competes partially with CO<sub>2</sub> for the adsorption centers. CO<sub>2</sub> adsorption capacity was recovered after removing the H<sub>2</sub>O from the gas inlet.

