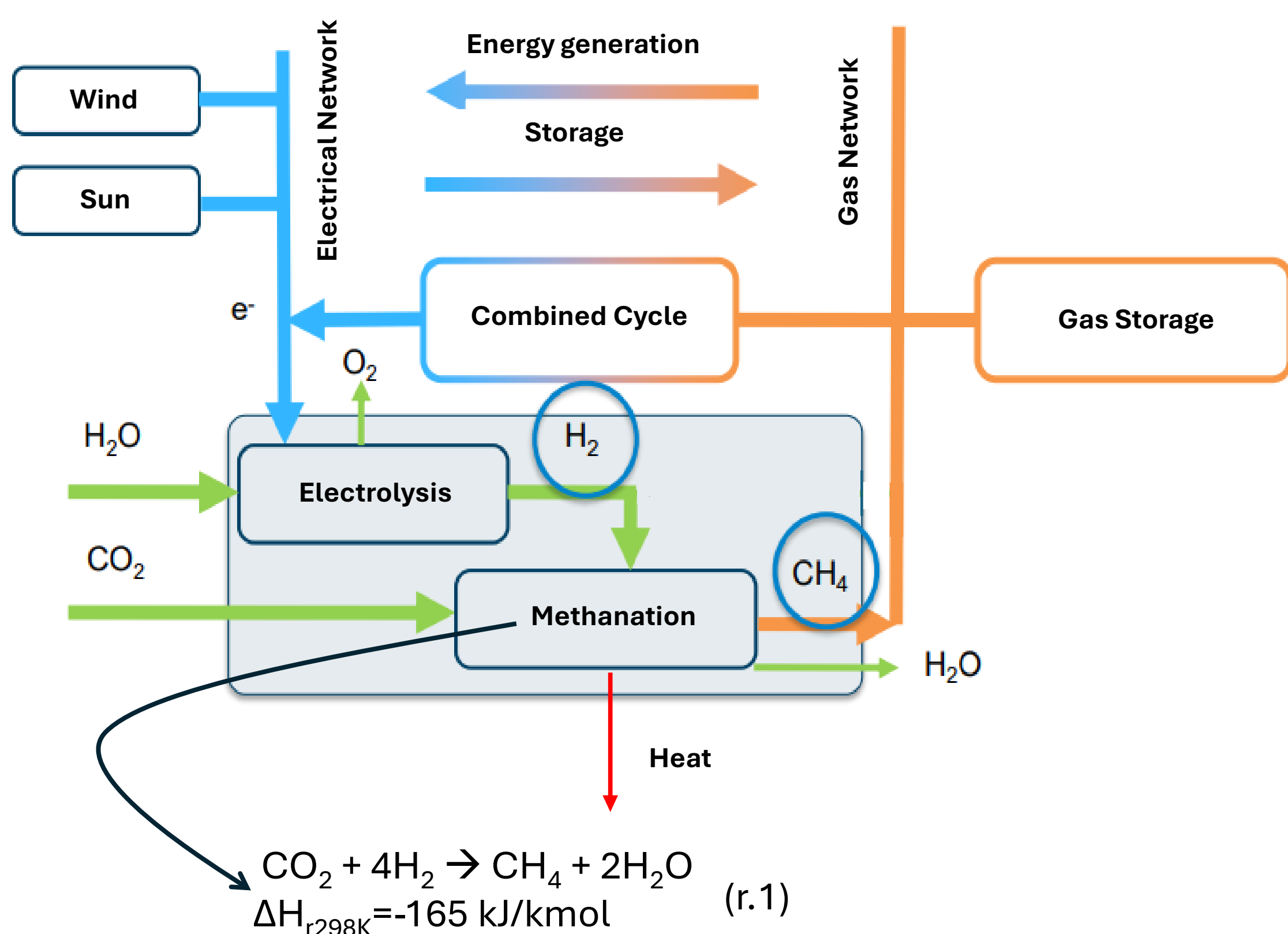


Different Behavior of Commercial Nickel and Ruthenium Catalysts in Biogas Upgrading

C. Gimeno-Izquierdo*, V. D. Mercader, P. Durán, P. Aragüés-Aldea, J. Á. Peña, J. Herguido

Catalysis and Reactor Engineering Group (CREG), Aragon Institute of Engineering Research (I3A), Zaragoza (Spain) email: 780111@unizar.es

INTRODUCTION



This work presents the results of CO₂ methanation in a fixed-bed reactor using the different catalysts listed in Table 1. The study involves the influence of temperature and the partial pressure of the reactant gases in the feed, serving as a preliminary step toward future experiments using real biogas under elevated pressure.

The experiments were conducted in a fixed-bed reactor (Figure 1) under the experimental conditions summarized in Table 2. CO₂ methanation proceeds via the Sabatier reaction (r. 1).

EXPERIMENTAL

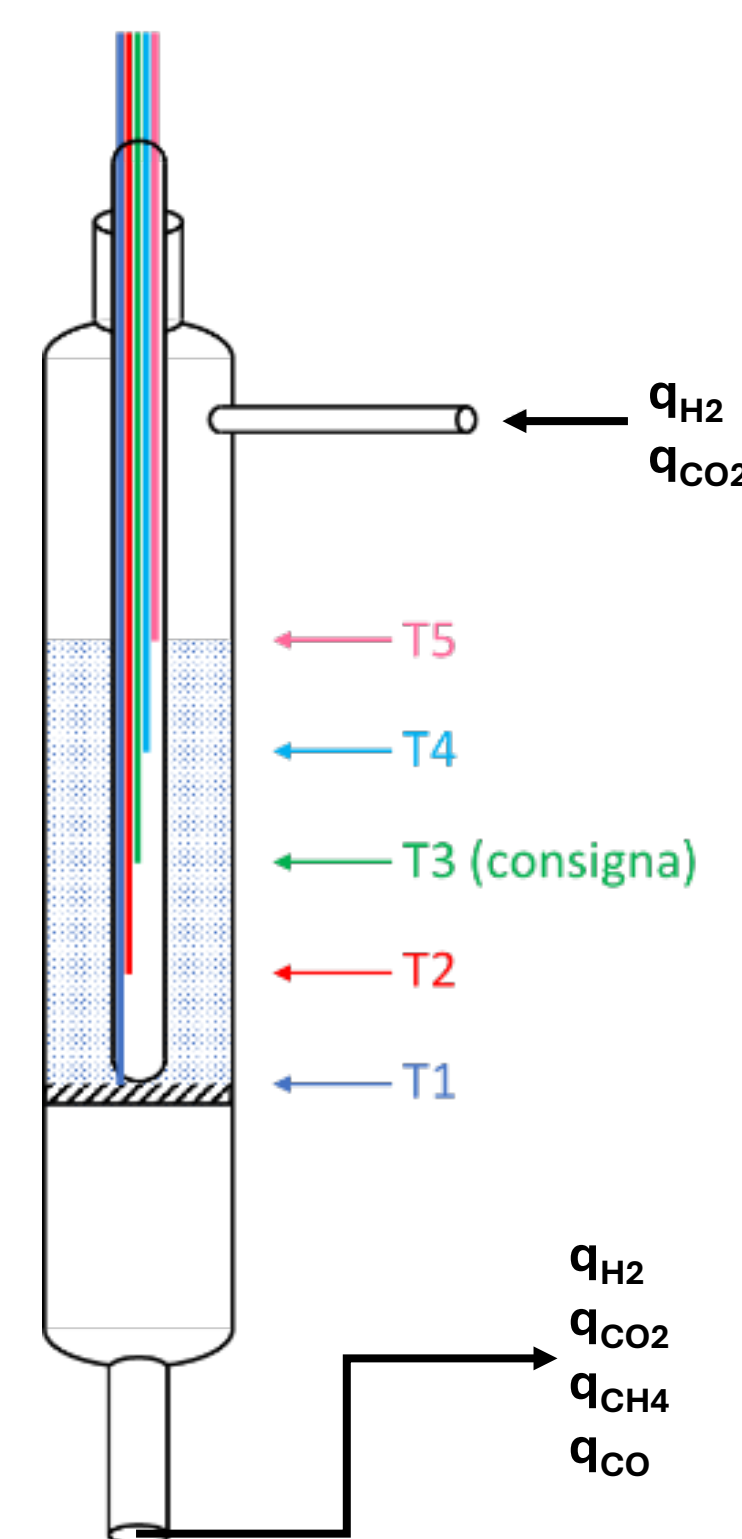


Figure 1. Schematic of the experimental reactor used

Table 1. Catalysts used throughout this work

Catalyst	Main Active Phase	φp (μm)
A	25 % ^w Nickel	100-200
B	20 % ^w Nickel	100-200
C	2 % ^w Ruthenium	2000
D	1.97 % ^w Ruthenium	2000

Table 2. Experimental conditions

Catalyst load (g)	0.5
Inert solid (SiC) load (g)	19
Temperature (°C)	250, 275, 300, 325, 350, 375, 400
H ₂ :CO ₂ ratio	2:1, 4:1, 6:1
Reactants:inerts ratio	9:1
Total volumetric flow (mLSTP/min)	250
Bed height (cm)	12
Reactor inner diameter (mm)	13
Thermocouple height (from the porous plate) (cm)	1, 3, 6, 9, 12

RESULTS

Table 3. SEM-based elemental mapping for catalysts A and B. Color intensity indicates a higher concentration of the element.

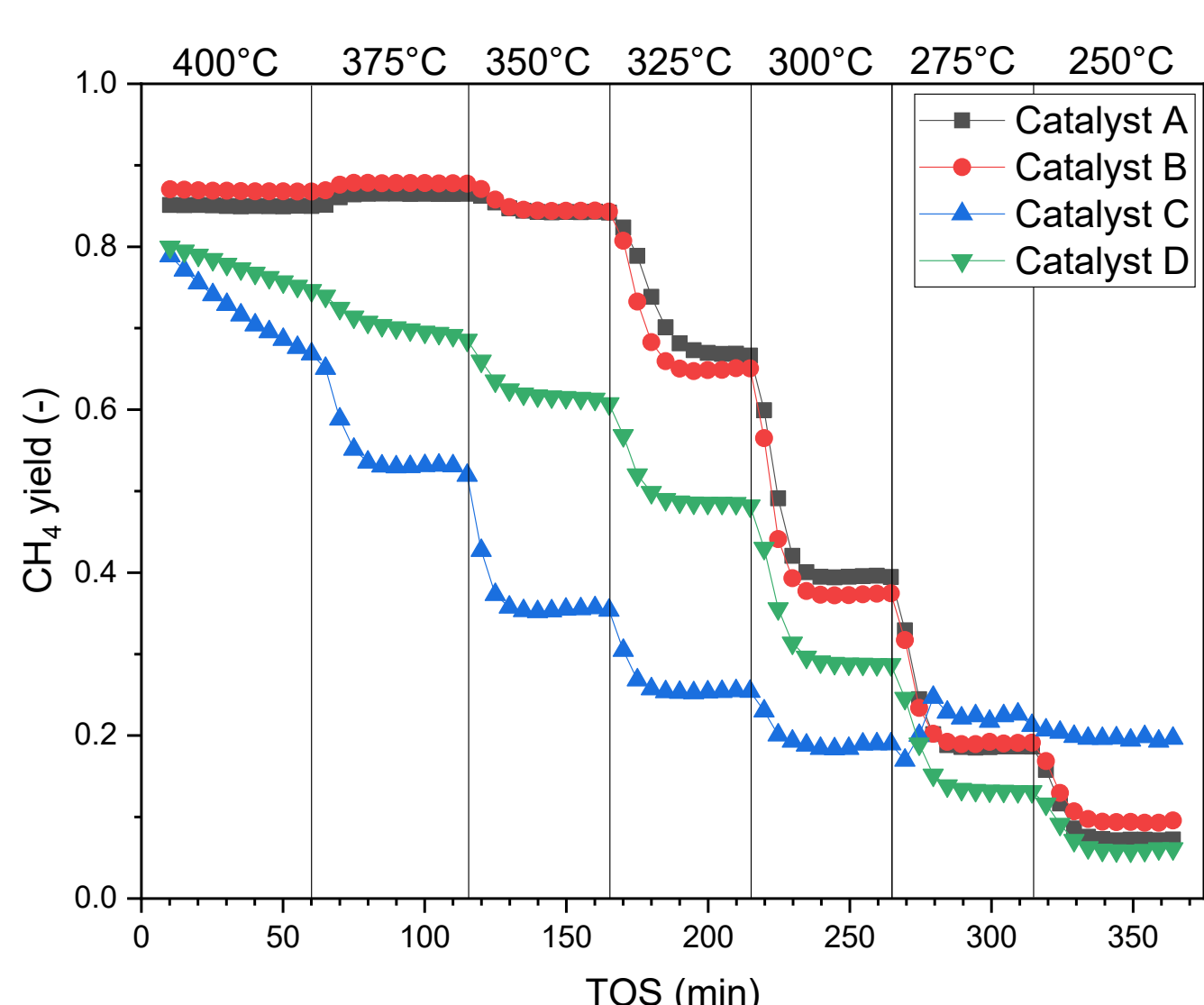


Figure 2. Methane yield vs time on stream (TOS) for the catalysts included in this study at different operating temperatures. The methane selectivity of the catalysts is close to unity at all temperatures.

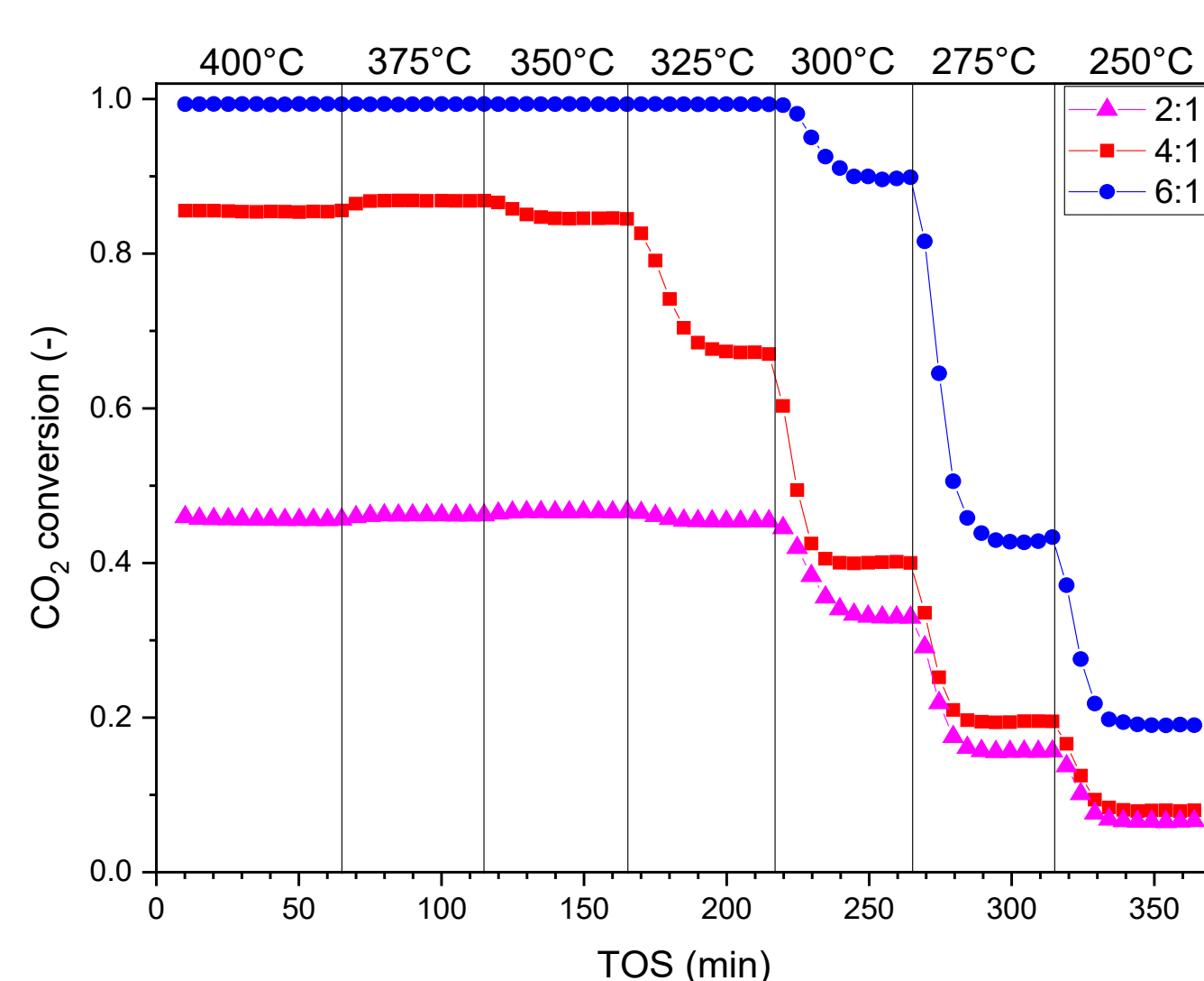


Figure 3. CO₂ conversion vs time on stream (TOS) for catalyst A at different H₂:CO₂ ratios.

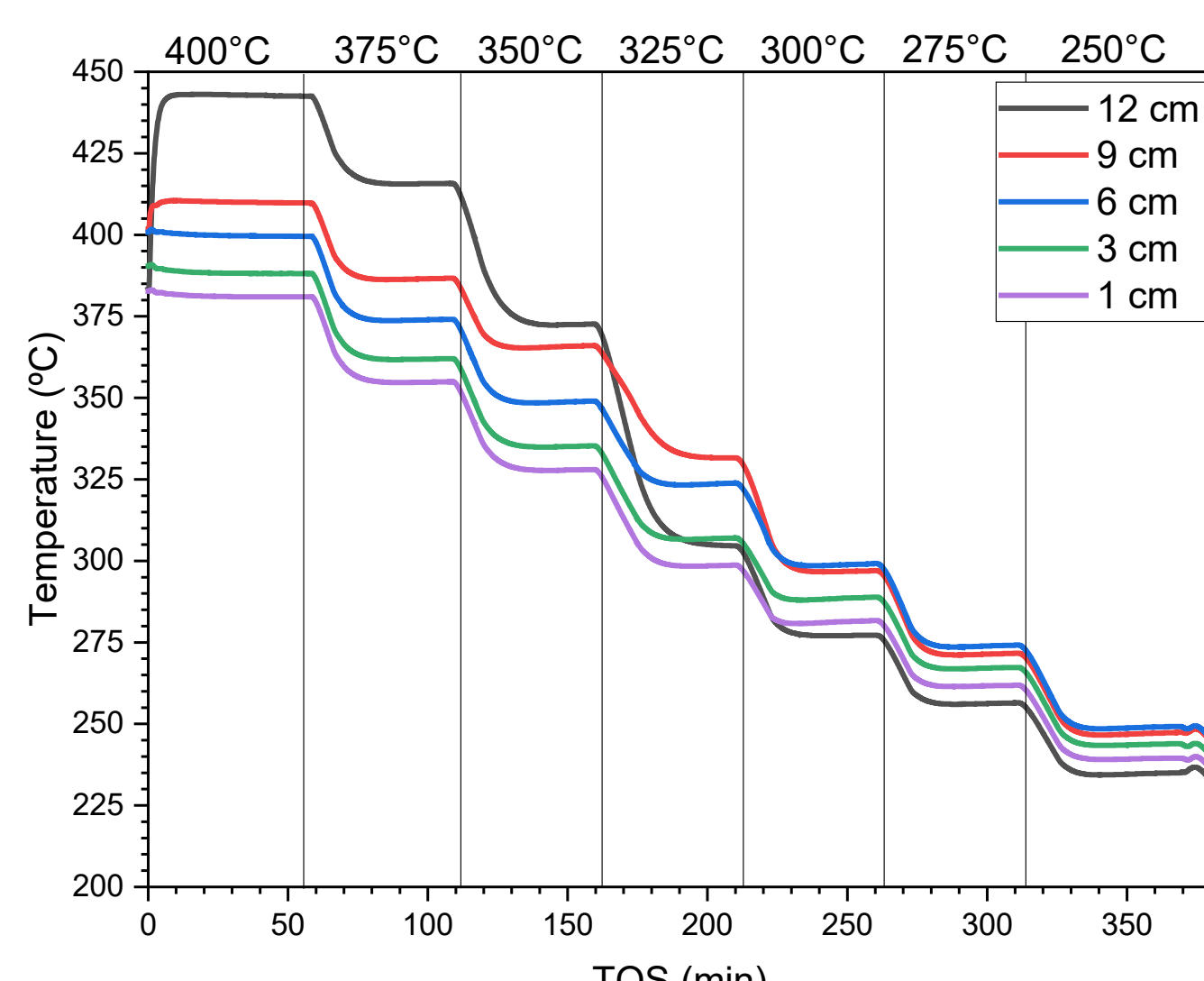


Figure 4. Temperature profile along the bed for catalyst A under stoichiometric reactant ratio during a test at different temperatures

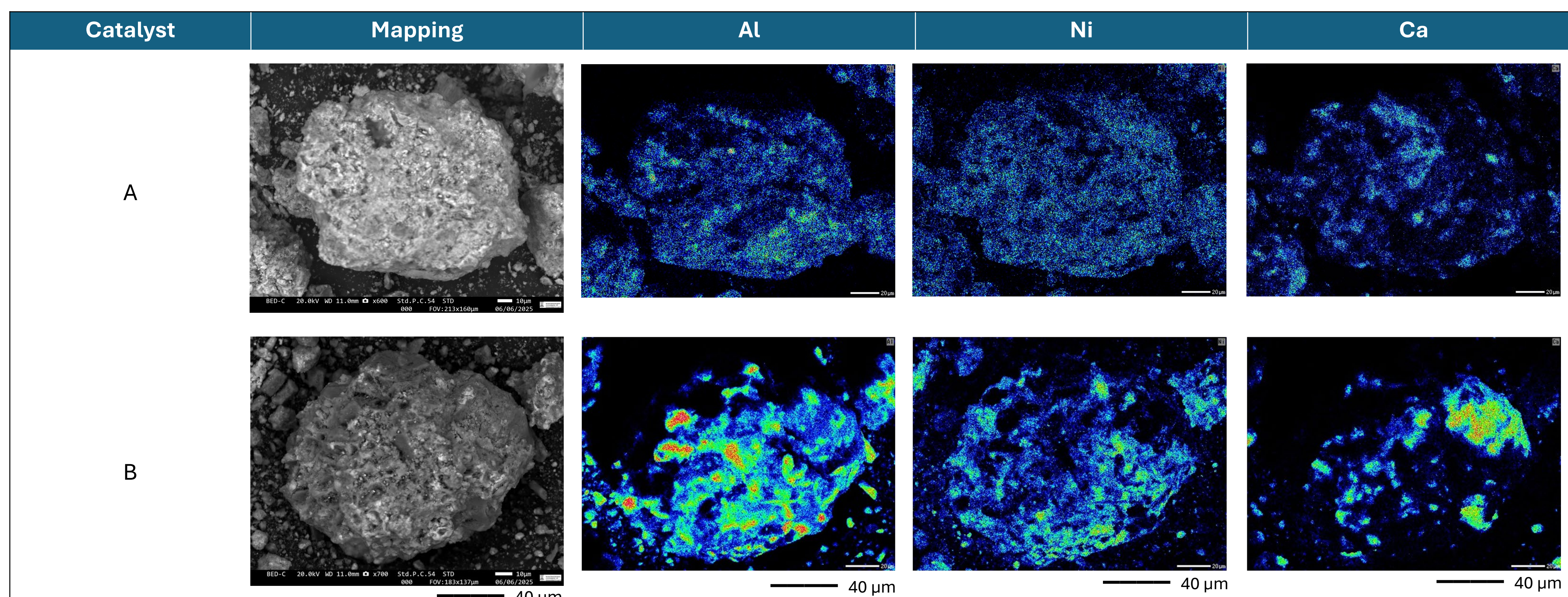


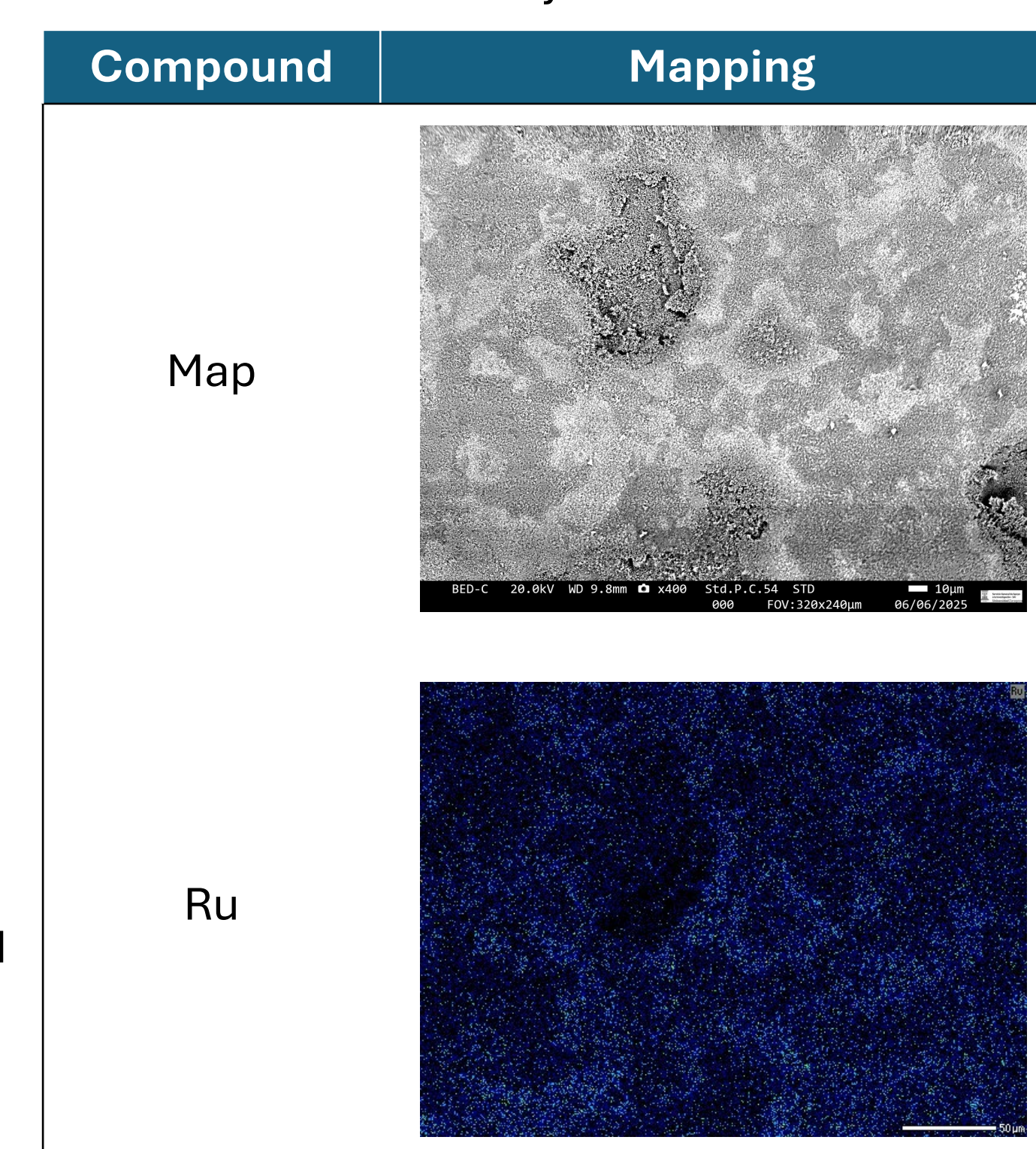
Table 4. Composition analysis of each catalyst by XRF

Catalyst	A	B	C	D
Ni	37.06	35.22	-	-
Al	24.21	54.74	96.77	93.85
Ca	15.76	8.08	-	0.20
Si	10.52	0.94	0.39	4.20
Fe	6.99	-	-	-
Na	-	0.30	-	-
Ru	-	-	0.88	0.97
Ce	-	-	1.76	-

Table 5. Specific surface area of the catalysts by the BET method

Catalyst	A	B	C	D
BET (m ² /g)	47.714	110.648	10.189	12.855

Table 6. SEM-based elemental mapping for catalysts C



CONCLUSIONS

The nickel-based catalysts (A and B) exhibited the highest activity, CO₂ conversion, and CH₄ yield. In contrast, the ruthenium-based catalysts (C and D) showed a significant deactivation, negatively affecting both conversion and methane yield. A positive effect on methane yields was observed when operating with an over-stoichiometric H₂:CO₂ ratio.

When analyzing the composition of the catalysts, it is observed that catalyst A has a slightly higher Ni content than catalyst B. Ru-based catalysts contain comparable Ru loadings. It is worth noting that catalyst C also contains Ce, which helps reduce coke deposits on the surface.

Nickel-based catalysts present a high specific surface area compared to that of the ruthenium-based ones. In that case, the much lower active surface area might be related to the fact that only the outer surface of the sphere is catalytically active.

As shown in Table 6, since the catalyst's active sites are located on the outer surface of the sphere, any detachment of this layer due to erosion or similar effects can result in the loss of the active phase, thereby reducing the overall catalytic activity.

REFERENCES

- CHEIN, R.Y. and WANG, C., 2020. Experimental Study on CO₂ Methanation over Ni/Al₂O₃, Ru/Al₂O₃, and Ru-Ni/Al₂O₃ Catalysts. *Catalysts*, 10 (2020) 1112. Available on: [doi:10.3390/CATAL10101112](https://doi.org/10.3390/CATAL10101112)
- MERCADER, V.D., DURÁN, P., ARAGÜÉS-ALDEA, P., FRANCÉS, E., HERGUIDO, J. and PEÑA, J.A. Biogas upgrading by intensified methanation (SESAR): Reaction plus water adsorption – desorption cycles with Ni-Fe/Al₂O₃ catalyst and LTA 5A zeolite. *Catalysis Today*, 433 (2024) 114667. Available on: [doi:10.1016/j.cattod.2024.114667](https://doi.org/10.1016/j.cattod.2024.114667).
- SANZ-MARTÍNEZ, A., DURÁN, P., MERCADER, V.D., FRANCÉS, E., PEÑA, J.A. and HERGUIDO, J., Biogas Upgrading by CO₂ Methanation with Ni-, Ni-Fe-, and Ru-Based Catalysts. *Catalysts* 12 (2022) 1609. Available on: [doi:10.3390/CATAL12121609](https://doi.org/10.3390/CATAL12121609)

ACKNOWLEDGEMENTS

Research funded by MICIU (Spanish *Ministerio de Ciencia, Innovación y Universidades*), *Agencia Estatal de Investigación* (AEI) project **PID2022-136947OB-I00** and *European Union Next Generation PRTR-C17.I1 Task LA4.A1*. The consolidated research group CREG (T43-23R) has received financial support from *Gobierno de Aragón* (Spain) through the European Social Fund – FEDER. This work was partially funded by the Scholarship and Grants Program of the Institute of Research in Engineering of Aragón (I3A).

