

Electronic supplementary information

Mono and bimetallic metal catalysts based on Ni and Ru supported on alumina coated
monoliths for CO₂ methanation

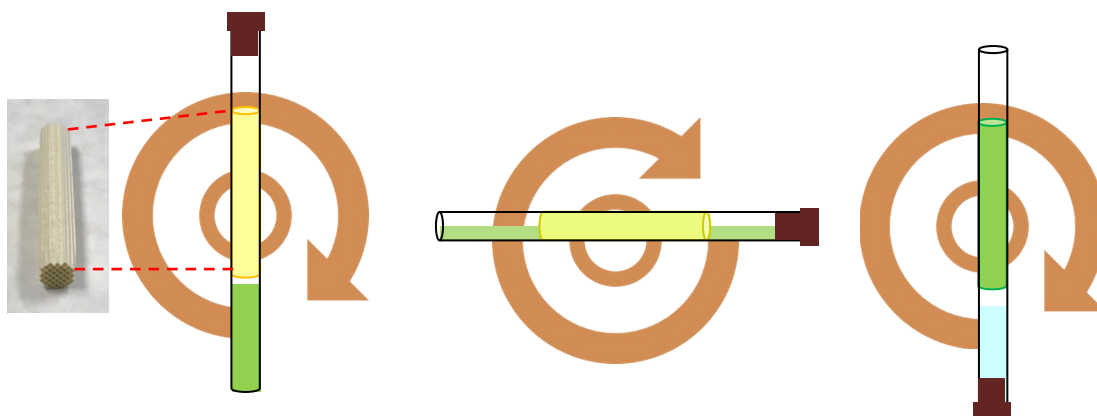
Ainhoa Bustinza¹, Marina Frías¹, Yuefeng Liu², Enrique García-Bordejé^{1*}

¹Instituto de Carboquímica (ICB-CSIC), Miguel Luesma Castán 4, E-50018 Zaragoza, Spain,

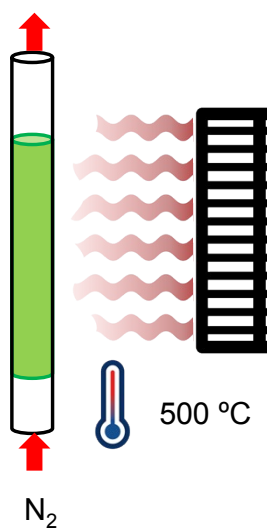
²Dalian National Laboratory for Clean Energy (DNL), Dalian Institute of Chemical Physics,
Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

* Corresponding author: Tel.: +34 976733977; fax.: +34 976733318 *E-mail address:* jegarcia@icb.csic.es

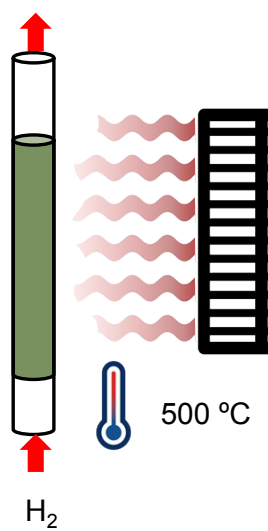
a) impregnation



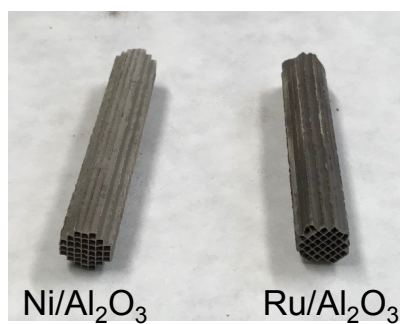
b) calcination



c) reduction



d)



Scheme 1. Illustration of the preparation steps

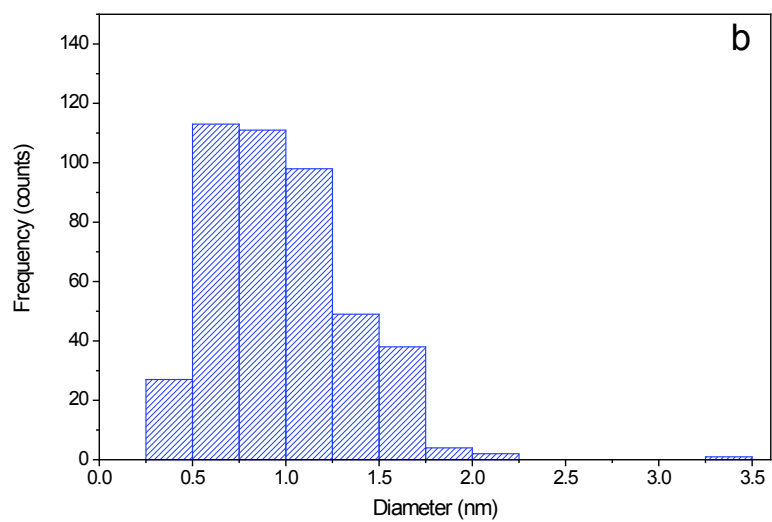
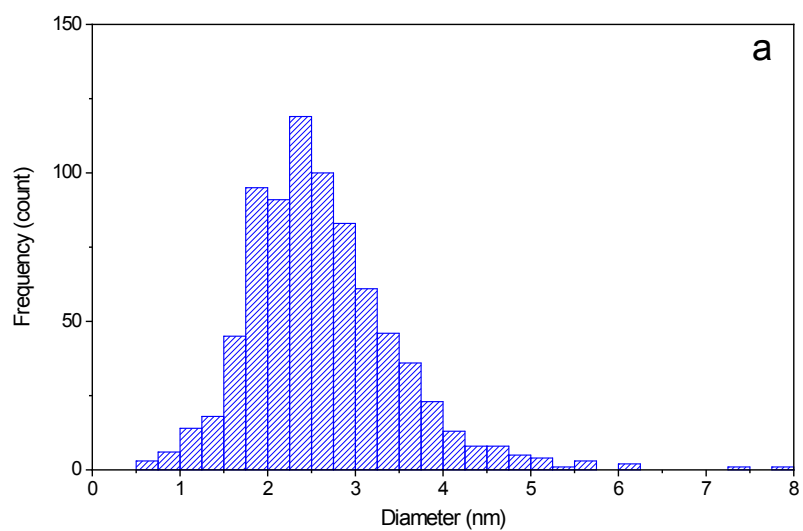


Figure S1. Particle size distribution for monometallic catalyst Ni (a) and Ru (b) derived from statistical analysis of HAADF-STEM images

Study of the effect of the internal and external mass transfer

The Weisz-Prater criteria was applied to assess the absence of mass transfer limitations, according to the following equations:

$$Ca = \frac{r_{CO_2} \cdot \rho_{cat}}{K_g \cdot a_m \cdot C_{CO_2}} < \frac{0,05}{n} \quad (\text{Equation 1})$$

$$WP = \frac{r_{CO_2} \cdot \rho_{cat} \cdot \delta_c^2}{D_{CO_2,e} \cdot C_{CO_2}} < \frac{n+1}{2} < 1 \quad (\text{Equation 2})$$

Where r_{CO_2} is the reaction rate, ρ_{cat} is the apparent catalytic layer density, K_g is the mass transfer coefficient, a_m is the geometric surface area, C_{CO_2} is the CO_2 concentration in the feed gas, δ_c is the characteristic dimension of the coating layer, $D_{CO_2,e}$ is the effective diffusion coefficient and n is the reaction order.

The parameters used in equation 1 and 2 are listed in Table S1. Some of these parameters were withdrawn from reference [S1] and the geometrical values of the monolith were withdrawn from [S2]. The characteristic dimension of the coating layer was an averaged value withdrawn from SEM images of alumina coated monoliths reported in our previous work [S3].

The values attained are $Ca=0,0033$ and $WP=1,6 \cdot 10^{-12}$ for the experimental conditions of $P=1$, $T=380$ °C and a flow-rate of 60 ml/min. Assuming a reaction order $n=0$ in agreement with literature ⁷, both criteria are met, confirming the absence of mass transfer limitations.

Table S1. Values of parameters used in equations 1 and 2.

Parameter	description	Units	Value
r_{CO_2}	CO_2 reaction rate	$Kmol \text{ kg}^{-1} \text{ s}^{-1}$	$8.51 \cdot 10^{-5}$
ρ_{cat}	True density of γ -alumina	$Kg \text{ m}^{-3}$	3650
K_g	mass transfer coefficient	m s^{-1}	1.01512
a_m	geometric surface area	$\text{m}^2 \text{ m}^{-3}$	2735.44
C_{CO_2}	CO_2 concentration in the feed gas	$Kmol \text{ m}^{-3}$	$3.98 \cdot 10^{-6}$
δ_c	characteristic dimension of the coating	m	$1.0 \cdot 10^{-6}$

	layer		
$D_{CO_2,e}$	effective diffusion coefficient	m^2s^{-1}	$7.73 \cdot 10^{-7}$
n	and n is the reaction order	-	0

References

S1. A. Vita A., C. Italiano, L. Pino L., P. Frontera , M. Ferraro, and V. Antonucci, *Appl. Catal. B: Environ.*, 2018, **226**, 384-395

S2. T. Vergunst, F. Kapteijn, J.A. and Moujin , *Ind. Eng. Res.* 2001, **40**, 2801-2809

S3. E. García-Bordejé, I. Kvande, D. Chen and M. Rønning, *Adv. Mater.*, 2006, **18**, 1589-1592.