

Supplementary materials

Wheat straw-derived activated biochar as a renewable support of Ni-CeO₂ catalysts for CO₂ methanation

Christian Di Stasi ^{a,*}, Simona Renda ^b, Gianluca Greco ^a, Belén González ^a, Vincenzo Palma ^b, Joan J. Manyà ^a

^a *Aragón Institute of Engineering Research (I3A), Thermochemical Processes Group, University of Zaragoza, Escuela Politécnica Superior, Crta. Cuarte s/n, 22071 Huesca, Spain*

^b *University of Salerno, Department of Industrial Engineering, Via Giovanni Paolo II 132, 84084, Fisciano (SA), Italy*

* Corresponding authors

E-mail addresses: christiandistasi@unizar.es (Christian Di Stasi)

Table S1. Summary of all the catalysts synthesized and tested in this work.

Sample ID	CeO ₂ , wt. %	Ni, wt. %	CO(NH ₂) ₂ , wt. %
BC	/	/	/
BCCe10Ni40	10	40	/
BCCe30Ni40	30	40	/
BCCe50Ni40	50	40	/
BCCe30Ni10	30	10	/
BCCe30Ni20	30	20	/
BCCe30Ni30	30	30	/
BCCe30Ni40	30	40	/
BCN50Ni20	/	20	50
BCN67Ni20	/	20	67
BCN75Ni20	/	20	75

Table S2. Proximate, ultimate, and inorganic matter analysis of the physically activated biochar (BC) employed as catalyst support.

Ultimate analysis (wt. %)	
Carbon	67.38
Hydrogen	1.12
Nitrogen	1.94
Oxygen ^a	29.56
Proximate analysis (wt. %)	
Moisture	N.D.
Volatiles	8.27
Ashes	41.92
Fixed Carbon ^a	50.72
Inorganic matter (wt. % in ash)	
SiO ₂	17.52
K ₂ O	16.68
CaO	7.40
P ₂ O ₅	2.45
MgO	1.51
Al ₂ O ₃	1.11
Fe ₂ O ₃	1.05
S	0.716
Cl	0.702
Na ₂ O	0.216

^a Values calculated by difference.

Table S3. Specific surface area (Langmuir, S_L) and pore volumes (V_{tot} , V_{micro} and V_{meso}) of BC, BCN75Ni20, and BCCe30Ni20 materials.

Sample	S_L	S_{micro} (m ² g ⁻¹)	S_{meso}	V_{tot}	V_{micro} (cm ³ g ⁻¹)	V_{meso}
BC	600	579	21.5	0.224	0.200	0.020
BCCe30Ni20	241	186	55.4	0.138	0.056	0.080
BCN75Ni20	310	278	31.7	0.135	0.090	0.040

Table S4. Surface composition measured by XPS and peak contributions of C1s, N1s, O1s and Ni2p for fresh and spent BCN75Ni20 catalyst —methanation experiment at 30 NL g⁻¹ h⁻¹, 400 °C and 1.00 MPa.

Sample	Surface concentration (at. %)			
	C1s	N1s	O1s	Ni2p
BC	81.1	2.0	16.9	—
BCN75Ni20	41.6	2.3	41.3	14.8
BCN75Ni20-spent	43.2	1.8	45.9	9.1

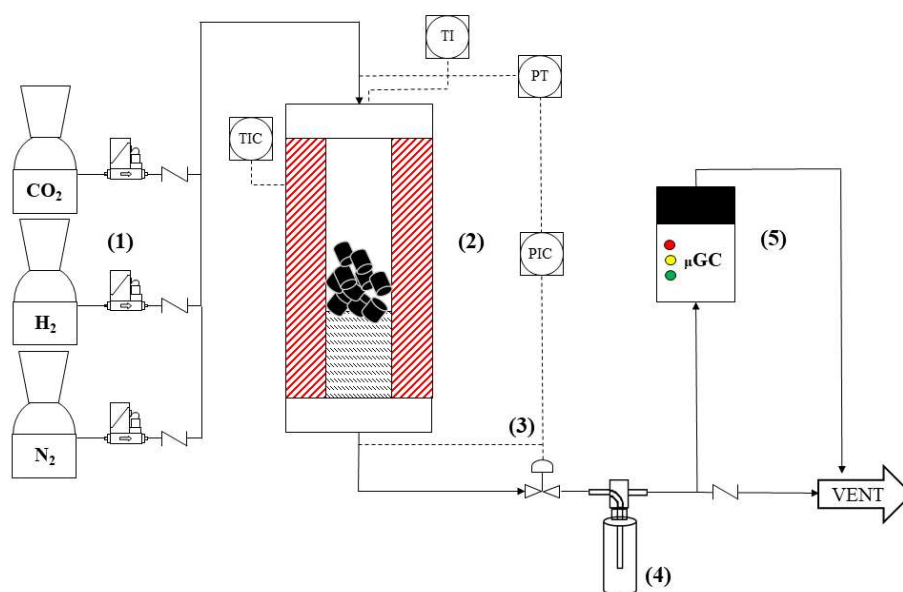


Figure S1. Schematic overview of the experimental device used in this work: feeding system (1); fixed-bed reactor and furnace (2); servo-controlled valve (3); water trap with CaCl_2 (4); and $\mu\text{-GC}$ analyzer (5).

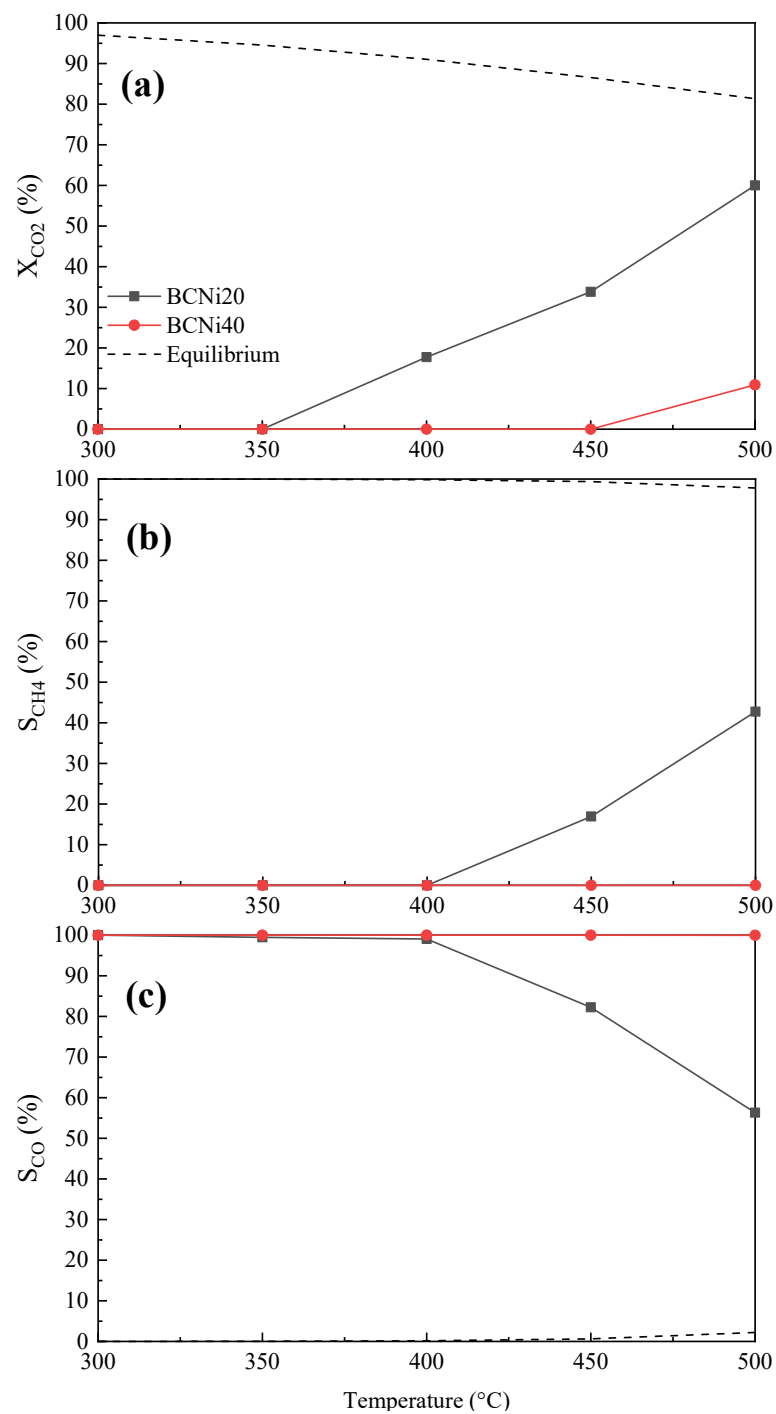


Figure S2. Results obtained during methanation experiments using the BCNi20 and BCNi40 catalysts at 1.0 MPa and 15 NL g⁻¹ h⁻¹.

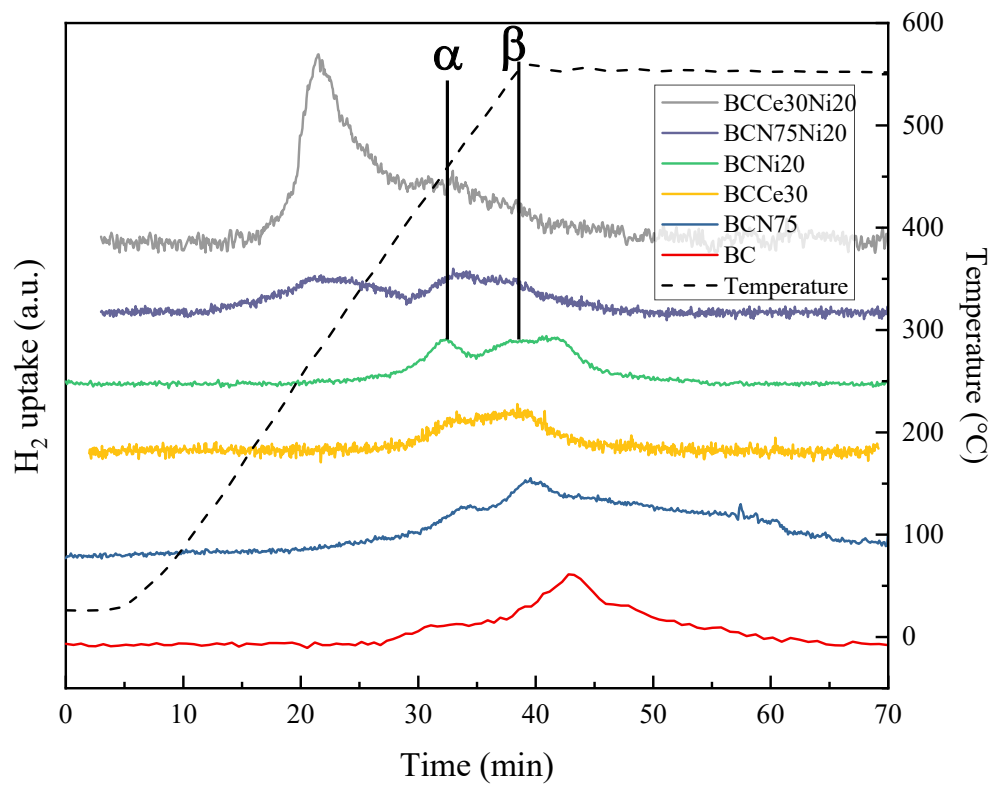


Figure S3. Hydrogen uptake profiles from TPR for different materials.

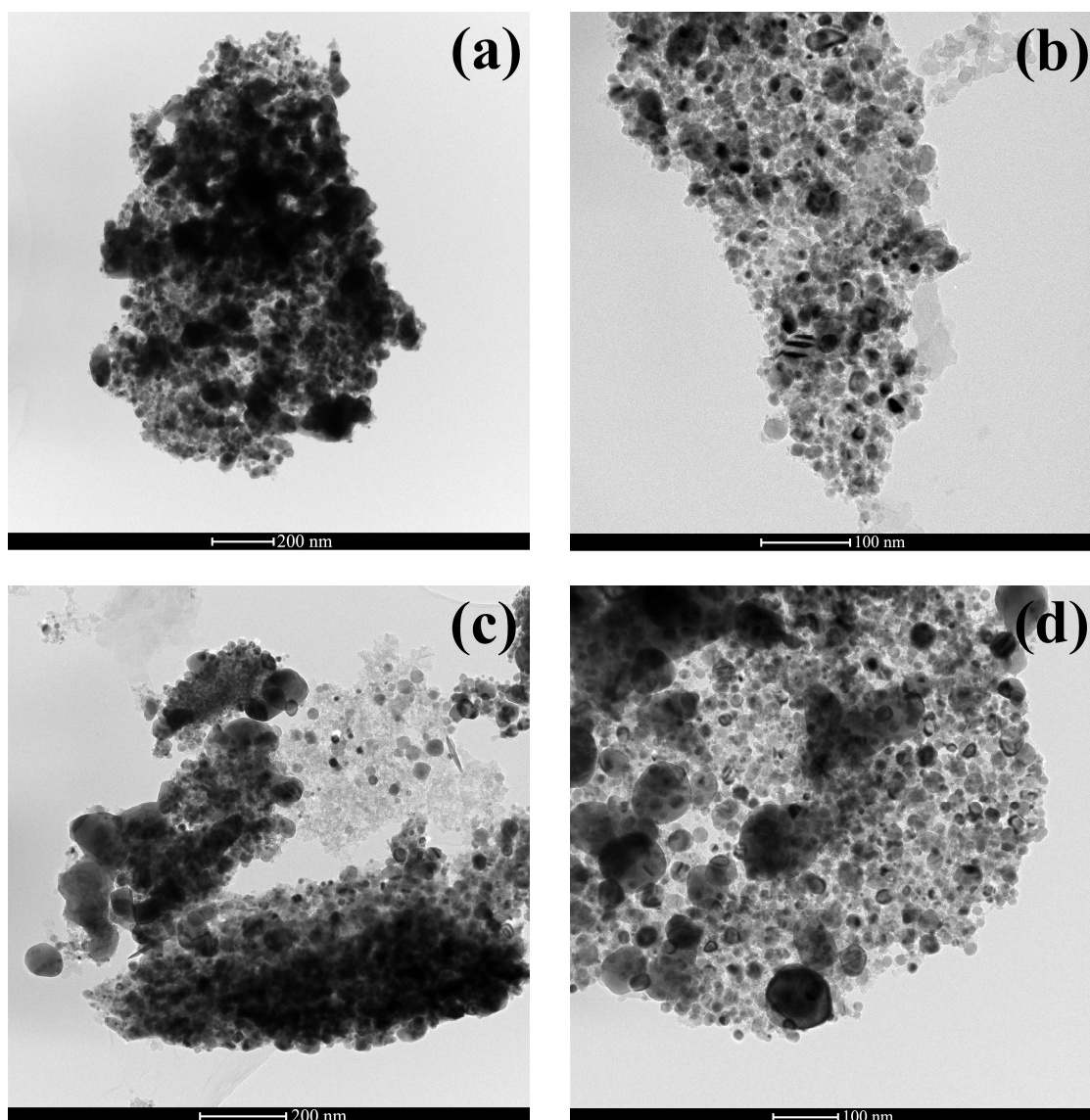


Figure S4. TEM images of BCN75Ni20 catalyst: fresh (a, b) and spent (c, d) after CO₂ methanation at 30 NL g⁻¹ h⁻¹, 400 °C and 1.0 MPa.

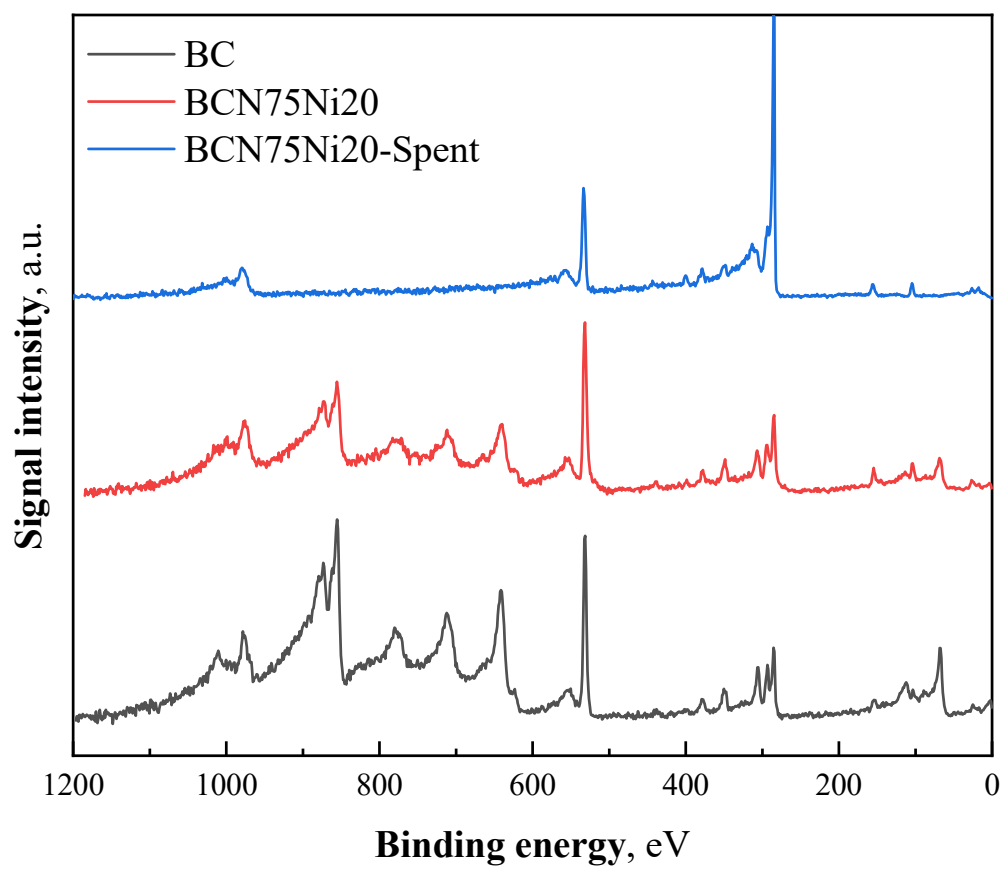


Figure S5. Full XPS spectra of BC, fresh BCN150Ni20, and spent BCN150Ni20 after CO₂ methanation at 30 NL g⁻¹ h⁻¹, 400 °C and 1.0 MPa.

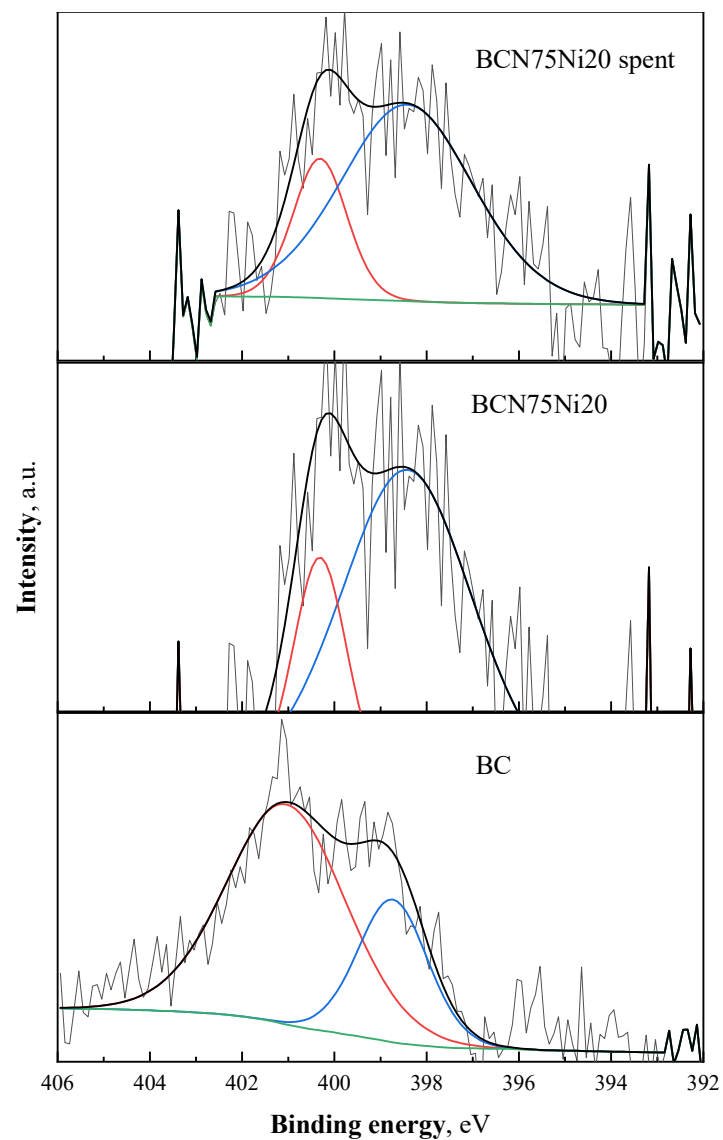


Figure S6. XPS high resolution spectra of N 1s of activated biochar (support), as well as fresh and spent BCN150Ni20 catalyst (CO_2 methanation at $30 \text{ NL g}^{-1} \text{ h}^{-1}$, 400°C and 1.0 MPa).

Nomenclature

d_p	Pore diameter (nm)
F_i	Molar flow rate (mol min ⁻¹)
S_i	Product selectivity (%)
S_L	Langmuir surface area (m ² g ⁻¹)
S_{meso}	Mesopores t-plot surface area (m ² g ⁻¹)
S_{micro}	Micropores t-plot surface area (m ² g ⁻¹)
V_{meso}	Volume of mesopores (cm ³ g ⁻¹)
V_{micro}	Volume of micropores (cm ³ g ⁻¹)
V_{tot}	Total pore volume (cm ³ g ⁻¹)
X_{CO_2}	Carbon dioxide conversion (%)

Acronyms

CHN	Ultimate analysis
GSV	Gas space velocity
GHSV	Gas hourly space velocity
NL	Fluid volume in liter evaluated at standard conditions according to IUPAC
NLDFT	Non-local density functional theory
NPs	Nanoparticles
PSD	Pore size distribution
PtG	Power-to-Gas
rWGS	Reverse water gas shift

TCD Thermal conductivity detector

TEM *Transmission electron microscopy*

TPR Temperature programmed reduction

XPS X-ray photoelectron spectroscopy

XRF X-ray fluorescence spectroscopy

μ-GC Micro gas chromatograph