Electronic Supplementary Information (ESI) for

# Upcycling Hazardous Waste into High-Performance Ni/η-Al<sub>2</sub>O<sub>3</sub> Catalysts for CO<sub>2</sub> Methanation

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## Supplementary note 1:

The surface area of an average spherical NiO particle (as shown in Fig. S5) with a 6.5 nm diameter was calculated based on the following equation

$$A = 4\pi r^2$$

r = sphere radius (3.25 nm) A = sphere surface area (132.7 nm<sup>2</sup>)

i. The volume of the average particle was obtained based on:

$$V = \frac{4}{3}\pi r^3$$

V= 143.8 nm<sup>3</sup> = 143.8e-21 cm<sup>3</sup> = 1.44e-19 cm<sup>3</sup> ρ = NiO density (6.67 g/cm<sup>3</sup>)

ii. The maass of the average particle was calculated using:

$$m = \rho * V$$

m = mass of the average NiO particle (9.6e-19 g)

iii. In the next step, the weight of NiO per gram of the catalyst was obtained:

$$m_{NiO} = \frac{\%_{Ni} * M_{NiO}}{M_{Ni}}$$

 $m_{NiO}$  = NiO mass (g) %<sub>Ni</sub> = Ni percentage (%)  $M_{NiO}$  = NiO molar mass (g/mol) (74.7 g/mol)  $M_{Ni}$  = Ni molar mass (g/mol) (58.7 g/mol)

iv. Given the obtained total NiO weight, the number of NiO particles per gram of catalyst was calculated:

$$N_{NiO} = \frac{m_{NiO}}{m}$$

 $N_{NiO}$  = number of NiO nanoparticles per gram catalyst (1.06e+17 for 8% Ni or 5.31e+16 for 4% Ni)

v. Finally, the total surface area of the NiO nanoparticles per gram catalyst was obtained:

$$SS_{NiO} = N_{NiO} * A$$

 $SS_{NiO}$  = NiO surface area (nm<sup>2</sup>) per gram catalyst (1.41e+17 nm<sup>2</sup> for 8% Ni or 7e+16 nm<sup>2</sup> for 4% Ni, 14.1 m<sup>2</sup> for 8% Ni or 7.0 m<sup>2</sup> for 4% Ni)

### Supplementary note 2:

#### Gas Hourly Space Velocity (GHSV) and Residence Time (τ)

To measure the interaction between the reactants  $(CO_2/H_2)$  and the catalyst bed in the reactor, it is necessary to calculate the gas hourly space velocity (GHSV). The GHSV describes the volume of reactants that passes through the catalyst bed per hour. Therefore, the total volumetric flow of the reactants, as well as the volume of the catalyst bed, are required for its calculation, as shown in the equation below,

$$GHSV = \frac{\dot{V}_{Reactants}}{V_{Catalyst}} = \frac{\dot{V}_{Reactants}}{\pi \cdot r^2 \cdot h}$$

GHSV = Gas Hourly Space Velocity (h<sup>-1</sup>)

 $\dot{V}_{Reactants}$  = Volumetric flow rate of reactants (0.75 L/h)  $V_{Catalyst}$  = Volume of catalytic bed (2.51 · 10<sup>-4</sup> L) r = internal radius of reactor (0.04 dm) h = height of catalytic bed (0.05 dm) GHSV = 2984.16 h<sup>-1</sup>

Moreover, the reciprocal value of the GHSV is the residence time ( $\tau$ ), so that

$$\tau = \frac{1}{GHSV} \cdot 3600$$

meaning that a reactant molecule spends 1.21 seconds over the catalyst bed before leaving the reactor.

#### Space-Time Yield (STY)

The space-time yield (STY) is another parameter used to characterize the performance of a catalyst. To determine this, the volume of the reagent gas is calculated according to equation **(S1)**, using the residence time and the gas flow rate. The molar amount of the product, assuming that it equals that of the reagent gas, is determined by rearranging the universal gas equation **(S2)**. The STY values are finally obtained by inserting the measured  $CH_4$  yield into equation **(S3)**.

$$V_{CO_2} = \dot{V}_{CO_2} \cdot \tau$$
 (S1)  
  $\dot{V}_{CO_2}$ = total gas flow of CO<sub>2</sub> (2.5 mL/min = 0.15 L/h)

 $\tau = residence time (0.0003 h)$ 

 $V_{CO_2}$  = volume of CO<sub>2</sub> (0.000050 L)

$$n_{CO_2} = \frac{p \cdot V_{CO_2}}{\mathbf{R} \cdot T} = n_{CH_4}$$
 (S2)

 $\begin{array}{l} p = \mbox{reaction pressure (1 atm = 1.01325 bar)} \\ R = \mbox{universal gas constant (0.083143 L·bar·mol^{-1}·K^{-1})} \\ T = \mbox{optimum reaction temperature (673 K)} \\ n_{CO_2} = \mbox{amount of CO}_2 (0.0000009 mol) \\ n_{CH_4} = \mbox{maximum amount of produced CH}_4 (0.0000009 mol = 0.0009102 mmol)} \end{array}$ 

$$STY = \frac{Yield \cdot n_{CH_4}}{100 \cdot m_{cat} \cdot \tau}$$
(S3)  
Yield = measured CH<sub>4</sub> yield (4-Ni/η-Al<sub>2</sub>O<sub>3</sub> - 16.09 %, 8-Ni/η-Al<sub>2</sub>O<sub>3</sub> - 59.16 %)  
 $n_{CH_4}$  = maximum amount of produced CH<sub>4</sub> (0.0009102 mmol)  
 $m_{cat}$  = mass of catalyst (0.02 g)  
 $\tau$  = residence time (0.0003 h)  
STY = space-time yield (4-Ni/η-Al<sub>2</sub>O<sub>3</sub> - 21.8562 mmol<sub>CH<sub>4</sub></sub> · g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup>, 8-Ni/η-Al<sub>2</sub>O<sub>3</sub> - 80.3460 mmol<sub>CH<sub>4</sub></sub> · g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup>)



**Supplementary Figure S1.** Illustration showing dissected inner components of a Ni-MH battery (top). Concentration (%) of elements detected by XRF spectrometry of NiSO<sub>4</sub> (precursor) recovered from cathode and mix of cathode and anode parts of spent Ni-MH battery (bottom).



**Supplementary Figure S2.** (a) Crystal structure of 4-Ni/η-Al<sub>2</sub>O<sub>3</sub> NCts before and after CO<sub>2</sub> methanation. (b) XRD comparison of 4 and 8-Ni/η-Al<sub>2</sub>O<sub>3</sub> NCts after CO<sub>2</sub> methanation. The two most intense peaks were used to calculate the average Ni crystallite size (see main text for details).



Supplementary Figure S3. HRTEM of  $\eta\text{-}Al_2O_3$  support.



Supplementary Figure S4. Rotational average plot of the  $\eta$ -Al<sub>2</sub>O<sub>3</sub> SAED (see inset of Fig. 1c, main text).



**Supplementary Figure S5.** Bright-field TEM images (top) of pristine  $4-Ni/\eta-Al_2O_3$  and  $8-Ni/\eta-Al_2O_3$  showing distribution of NiO within the  $\eta-Al_2O_3$  matrix. The NiO in  $\eta-Al_2O_3$  was identified based on the Ni L-edge using EELS (bottom).



Supplementary Figure S6. TEM images demonstrating the homogenous Ni particle size and distribution in 4 and  $8-Ni/\eta-Al_2O_3$  after CO<sub>2</sub> methanation.



Supplementary Figure S7. EELS spectra corresponding to Ni  $L_{3,2}$ -edges of 4-Ni/ $\eta$ -Al<sub>2</sub>O<sub>3</sub> and 8-Ni/ $\eta$ -Al<sub>2</sub>O<sub>3</sub> after CO<sub>2</sub> methanation.



Supplementary Figure S8. BET surface area and BJH pore size analysis of 4, 8-Ni/ $\eta$ -Al<sub>2</sub>O<sub>3</sub>, and  $\eta$ -Al<sub>2</sub>O<sub>3</sub>.

**Supplementary Table S1.** Comparison of STY ( $mmol_{CH_4}$ .  $g_{Ni}^{-1}$ . h<sup>-1</sup>) of best performing NCts (8-Ni/η-Al<sub>2</sub>O<sub>3</sub>) with Ni-based NCts from literature.

Materials description	Synthesis method	Catalytic conditions				efs.
		Pretreatment	Reaction (Gases%)	Pressure/ Temp.	Normalized STY $mmol_{CH_4}$ . $g_{\rm Ni}^{-1}$ . h <sup>-1</sup>	Supp. Re
Ni-siliceous MCM-41	Hydrothermal Method	Reduced in pure H₂ at 700 °C for 0.5 h	H <sub>2</sub> :CO <sub>2</sub> = 2.6:1	1.01325 bar /400°C	1315.46	1
Ni-CeO <sub>2</sub> nanorods	Hydrothermal Method	None	H <sub>2</sub> :CO <sub>2</sub> = 4	1 bar /275°C	154.31	2
Ni- Microporous Graphene like Carbon	Incipient wetness impregnation method	Reduced in pure H₂ at 400 °C for 2 h	H <sub>2</sub> :CO <sub>2</sub> :N <sub>2</sub> = 4:1:1	1.01325 bar /400°C	858.69	3
Ni-Zn/SiO <sub>2</sub>	Ammonia evaporation process	Reduced in pure H <sub>2</sub> at 500 °C for 3 h	H <sub>2</sub> :CO <sub>2</sub> = 4	1.01325 bar /230°C	13.77	4
5-Ni/ZrO₂	Incipient wetness impregnation method	Reduced in pure H <sub>2</sub> at 500 °C for 5 h	H <sub>2</sub> :CO <sub>2</sub> :N <sub>2</sub> = 4:1:5	10 bar /300°C	189.51	5
Ni-zeolite from coal gangue	Wet impregnation	Reduced in pure H₂ at 500 °C for 1 h	15% CO <sub>2</sub> , 60% H <sub>2</sub> , and 25% Ar (molar basis)	1 bar /450°C	98.98	6
Ni/Mn-CeO <sub>2</sub>	Sol-gel method	Reduced in pure H <sub>2</sub> at 550 °C for 2 h	H <sub>2</sub> :CO <sub>2</sub> = 4	1.01325 bar /370°C	188.34	7
Ni- MgO/MgH <sub>2</sub>	Mechanochemica I ball-milling method	Reduced in H <sub>2</sub> /N <sub>2</sub> gas (20% H <sub>2</sub> ) at 380 °C for 5 h	H <sub>2</sub> :CO <sub>2</sub> = 4	10 bar /300°C	68.85	8
8-Ni/η-Al <sub>2</sub> O <sub>3</sub>	Battery waste- upcycling	Reduced in 5% H <sub>2</sub> at 550 °C for 30 min.	5% CO <sub>2</sub> , 20% H <sub>2</sub> , and 75% Ar	1 bar /400°C	1004.32	This work

# **Supplementary References**

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