Supplementary Information for "Carbon nanostructure formation over Ni, Co, Fe on γ-Al_2O_3 during low-temperature dry reforming of methane: insights into mechanisms and catalytic behaviour"

Results and discussion

Characterisation of the products

Analysis of the carbon species

Table S1. Carbon balance for Ni/γ-Al_2O_3 at 500 °C.

τ, min	X_{CH4}, %	X_{CO2}, %	Y_{CO}, %	Y_{H2}, %	$r_{H2/CO}$
0	68.19	42.76	12.48	16.60	1.33
15	63.45	46.34	13.95	16.44	1.18
45	62.78	44.73	12.63	16.01	1.27
75	62.87	43.20	11.61	15.37	1.32
105	62.75	42.34	10.98	15.44	1.41
135	62.66	42.73	10.35	15.26	1.47

Carbon closure: 64.21%

Carbon inlet (gas): 167.31 mmol

Carbon outlet (gas): 97.78 mmol

Carbon outlet (deposit): 9.64 mmol

Table S2. Carbon balance for Ni/γ-Al_2O_3 at 600 °C.

τ, min	X_{CH4}, %	X_{CO2}, %	Y_{CO}, %	Y_{H2}, %	$r_{H2/CO}$
0	79.52	64.07	23.71	21.20	0.89
15	73.83	63.13	22.31	20.09	0.90
45	75.08	62.27	21.35	20.54	0.96
75	75.59	61.29	20.79	20.72	1.00

105	75.77	60.76	20.39	20.82	1.02
135	75.78	60.06	19.93	20.37	1.02

Carbon closure: 59.40%

Carbon inlet (gas): 167.31 mmol

Carbon outlet (gas): 87.84 mmol

Carbon outlet (deposit): 11.54 mmol

Table S3. Carbon balance for Co/γ-Al_2O_3 at 500 °C.

τ, min	X_{CH_4}, %	X_{CO_2}, %	Y_{CO}, %	Y_{H_2}, %	$r_{H_2/CO}$
0	80.62	56.03	19.44	20.07	1.03
15	78.50	58.20	19.27	20.11	1.04
45	77.28	59.06	19.26	20.05	1.04
75	77.03	58.90	19.28	19.71	1.02
105	76.65	59.11	19.21	19.68	1.02
135	76.42	59.20	19.12	19.87	1.04

Carbon closure: 58.35%

Carbon inlet (gas): 167.31 mmol

Carbon outlet (gas): 85.67 mmol

Carbon outlet (deposit): 11.95 mmol

Table S4. Carbon balance for Co/γ-Al_2O_3 at 600 °C.

τ, min	X_{CH_4}, %	X_{CO_2}, %	Y_{CO}, %	Y_{H_2}, %	$r_{H_2/CO}$
0	79.45	69.37	25.71	24.02	0.93
15	75.44	68.22	25.50	23.68	0.93
45	73.35	65.44	23.66	22.74	0.96
75	73.74	60.82	21.36	22.32	1.05
105	73.48	58.88	19.92	21.72	1.09

135	72.89	57.21	19.18	21.67	1.13

Carbon closure: 61.87%

Carbon inlet (gas): 167.31 mmol

Carbon outlet (gas): 90.16 mmol

Carbon outlet (deposit): 13.36 mmol

Table S5. Carbon balance for Fe/γ-Al_2O_3 at 500 °C.

τ, min	X_{CH4}, %	X_{CO2}, %	Y_{CO}, %	Y_{H2}, %	$r_{H2/CO}$
0	7.89	5.99	10.32	4.50	0.44
15	4.08	5.09	6.93	3.98	0.57
45	3.48	5.28	0.78	3.60	4.61
75	3.39	4.47	0.84	3.64	4.35
105	2.67	3.95	0.84	3.66	4.36
135	1.78	3.26	0.88	3.65	4.16

Carbon closure: 98.23%

Carbon inlet (gas): 167.31 mmol

Carbon outlet (gas): 164.35 mmol

Carbon outlet (deposit): 0.00 mmol

Table S6. Carbon balance for Fe/γ-Al_2O_3 at 600 °C.

τ, min	X_{CH4}, %	X_{CO2}, %	Y_{CO}, %	Y_{H2}, %	$r_{H2/CO}$
0	10.33	10.54	0.46	3.75	8.20
15	9.49	9.94	0.47	3.36	7.18
45	8.84	9.54	0.49	3.34	6.85
75	7.33	8.33	0.48	3.40	7.01
105	6.97	8.08	0.47	3.37	7.13
135	5.94	7.46	0.53	3.44	6.55

Carbon closure: 92.28%

Carbon inlet (gas): 167.31 mmol

Carbon outlet (gas): 154.40 mmol

Carbon outlet (deposit): 0.00 mmol

Experimental section

Analytical and experimental techniques

Catalytic measurements

The reactant conversion, product selectivity and yield were calculated on the basis of the peak areas obtained by GC–TCD, using the internal standard method, whereby Ar served as the internal reference. This approach accounts for changes in the total molar flow rate arising from the non-equimolar stoichiometry of the carbon-forming side reactions, and eliminates the need for a separate outlet flow measurement.

The relative response factors (RF_i) were determined from dedicated calibration injections performed prior to each catalytic experiment. For CH_4 and CO_2, RF was derived from injections of the reaction gas mixture (25% CH_4 – 25% CO_2/Ar), while for CO and H_2 – from injections of the respective pure gases (100% CO, 100% H_2), with peak areas corrected for dilution relative to the reaction gas mixture:

$$RF_i = \frac{A_{Ar}^{ref}}{A_i^{ref}} \times \frac{x_i^{in}}{x_{Ar}} \quad (1)$$

$\mathbf{A^{ref}_{Ar}}$ – median peak area of Ar from three replicate calibration injections;

$\mathbf{A^{ref}_{i}}$ – median peak area of component *i* (CH_4, CO_2, CO or H_2) from three replicate calibration injections;

$\mathbf{x^{in}_{i}}$ – mole fraction of component *i* in the feed (0.25 for CH_4 and CO_2, 1.0 for CO and H_2);

$\mathbf{x_{Ar}}$ – mole fraction of Ar in the feed (0.5).

The mole fraction of each component (CH_4, CO_2, CO, H_2) in the reactor outlet (x^{out}_i) was calculated as:

$$x_i^{out} = \frac{A_i^{exp}}{A_{Ar}^{exp}} \times x_{Ar} \times RF_i \quad (2)$$

$\mathbf{A^{exp}_{i}}$ – experimental peak area of component *i* (CH_4, CO_2, CO, H_2);

$\mathbf{A^{exp}_{Ar}}$ – experimental peak area of Ar.

The conversions of CH_4 and CO_2 (X_i) were calculated as:

$$X_i = \left(1 - \frac{x_i^{out}}{x_i^{in}}\right) \times 100 \tag{3}$$

$\mathbf{x^{in}_i}$ – mole fraction of component *i* in the feed (0.25 for CH_4 or CO_2).

The selectivities of CO and H_2 (S_i) were defined with respect to the stoichiometry of the main DRM reaction, in which one mole of consumed CH_4 can yield a maximum of two moles of each product:

$$S_i = \frac{x_i^{out}}{2 \times \Delta x_{CH_4}} \times 100 \tag{4}$$

$$\Delta x_{CH_4} = x_{CH_4}^{in} - x_{CH_4}^{out} \tag{5}$$

$\mathbf{\Delta x_{CH4}}$ – consumed mole fraction of CH_4.

The yields of CO and H_2 (Y_i) were obtained as:

$$Y_i = \frac{X_{CH_4} \times S_i}{100} \tag{6}$$

The H_2/CO molar ratio in the outlet ($r_{H2/CO}$) was determined as:

$$r_{H_2/CO} = \frac{x_{H_2}^{out}}{x_{CO}^{out}} \tag{7}$$

Characterisation of the products

The carbon balance was established to quantify the distribution of inlet carbon between the gas phase and solid deposits on the catalytic system during the catalytic measurements.

The molar flow rate of Ar (F_{Ar}) was calculated as:

$$F_{Ar} = \frac{F^{in} \times x_{Ar}}{V_m} \times 1000 \tag{8}$$

F^{in} – total inlet volumetric flow rate (50.0 mL/min);

V_m – molar volume at STP (22.414 mL/mol).

Since Ar is chemically inert under the reaction conditions, F_{Ar} remains constant throughout the experiment and serves as the reference flow for all molar calculations.

The inlet molar flow rates of CH_4 and CO_2 (F^{in}_i) were obtained as:

$$F^{in}_i = F_{Ar} \times \frac{x^{in}_i}{x_{Ar}} \tag{9}$$

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x^{in}_i – mole fraction of component *i* in the feed (0.25 for CH_4 or CO_2);

x_{Ar} – mole fraction of Ar in the feed (0.5).

The total amount of carbon supplied to the reactor over the catalytic measurements (n^{in}_C) was:

$$n^{in}_C = \left(F^{in}_{CH_4} + F^{in}_{CO_2}\right) \times \tau \tag{10}$$

τ – duration of the experiment (150 min).

The instantaneous molar flow rate of carbon in the outlet gas at measurement point ($F_{\tau k}{}^{out}{}_{Cgas}$) was calculated as:

$$F_{\tau_k}{}^{out}_{C_{gas}} = \frac{F_{Ar}}{x_{Ar}} \times \left(x^{out}_{CH_4} + x^{out}_{CO_2} + x^{out}_{CO}\right)_{\tau_k} \tag{11}$$

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x^{out}_{CH4}, x^{out}_{CO2}, x^{out}_{CO} – mole fraction of CH_4. CO_2. CO in the reactor outlet;

τ_k – measurement point of the experiment (0, 15, 45, 75, 105, 135 min).

H_2 does not contain carbon and was therefore excluded from the expression.

The total carbon recovered in the gas phase over the catalytic measurements (n^{out}_{Cgas}) was obtained by trapezoidal integration over the six measurement points (τ_k = 0, 15, 45, 75, 105, 135 min), with the value at τ of 150 min цфы extrapolated from the previous ones:

$$n^{out}_{C_{gas}} = \sum_k \frac{F_{\tau_k}C^{out}_{gas} + F_{\tau_{k+1}}C^{out}_{gas}}{2} \times \left(\tau_{k+1} - \tau_k\right) \tag{12}$$

τ_{k+1} – next measurement point of the experiment (15, 45, 75, 105, 135, 150 min).

The mass of solid carbon deposited on the spent catalyst (m^{out}_{Csol}) was derived from the mass fraction of carbon in the spent catalyst sample obtained by TOC (w^{out}_C) as:

$$m^{out}_{C_{sol}} = \frac{w^{out}_{C_{sol}} \times m_{cat}}{1 - w^{out}_{C_{sol}}} \tag{13}$$

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m_{cat} – initial catalyst mass (0.50 g).

This formulation correctly accounts for the fact that the TOC instrument measures w^{out}_C as the carbon fraction in the total mass of the spent sample.

The molar amount of the solid carbon deposited (n^{out}_{Csol}) was then:

$$n^{out}_{C_{sol}} = \frac{m^{out}_{C_{sol}}}{M_C} \times 1000 \tag{14}$$

M_C – molar mass of C (12.011 g/mol).

Carbon balance closure (CB) and carbon deposition efficiency (CDE) were defined as:

$$CB = \frac{n^{out}_{C_{gas}} + n^{out}_{C_{sol}}}{n^{in}_C} \times 100 \tag{15}$$

$$CED = \frac{n^{out}_{C_{sol}}}{n^{in}_C} \times 100 \tag{16}$$