Supplementary information

Table S1. Nickel catalysts reported for CO_2 hydrogenation at atmospheric pressure.

Catalyst	Molar ratio H_2:CO_2:N_2*	Temp. °C	GHSV	x_{CO2} %	S_{CH4} %	Ref.
5%Ni/SiO_2	4:1:1.1	350	11,000 h^{-1}	38	90.0	[2]
5%Ni/CZ $_{imp}$	4:1:1.1	350	43,000 h^{-1}	60	97.3	
5%Ni/CZ $_{sol–gel}$	4:1:1.1	350	43,000 h^{-1}	80	90.0	
5%NiUSY$_{Imp}$	4:1:1.1	400	43,000 h^{-1}	24.7	61.4	[3]
4%Ni3%CeUSY$_{Imp}$	4:1:1.1	400	43,000 h^{-1}	37.7	72.1	
4%Ni7%CeUSY$_{Imp}$	4:1:1.1	400	43,000 h^{-1}	44.3	75.5	
5%Ni15%CeUSY$_{Imp}$	4:1:1.1	400	43,000 h^{-1}	55.0	86.2	
10%NiUSY$_{Imp}$	4:1:1.1	400	43,000 h^{-1}	47.9	78.8	
8%Ni7%CeUSY$_{Imp}$	4:1:1.1	400	43,000 h^{-1}	51.7	85.6	
14%NiUSY$_{Imp}$	4:1:1.1	400	43,000 h^{-1}	65.5	94.2	
14%Ni7%CeUSY$_{Imp}$	4:1:1.1	400	43,000 h^{-1}	68.3	95.1	
5%Ni/$80Ce_{20}Zr$	4:1:1.1	350	43,000 h^{-1}	71.5	98.5	[5]
5%Ni/$60Ce_{40}Zr$	4:1:1.1	350	43,000 h^{-1}	79.7	99.3	
5%Ni/$20Ce_{80}Zr$	4:1:1.1	350	43,000 h^{-1}	73.0	99.0	
(5%Ni–0.5%Rh)/ 80Ce20Zr	4:1:1.1	350	43,000 h^{-1}	77.8	99.2	
15%Ni/Al_2O_3	4:1:0	350	15,000 ml g^{-1} h^{-1}	45.0	100.0	[6]
15%Ni-0.3%CeO_2/Al_2O_3	4:1:0	350	15,000 ml g^{-1} h^{-1}	55.0	98.0	
15%Ni-0.5%CeO_2/Al_2O_3	4:1:0	350	15,000 ml g^{-1} h^{-1}	65.0	99.0	
15%Ni-2%CeO_2/Al_2O_3	4:1:0	350	15,000 ml g^{-1} h^{-1}	71.0	100.0	
15%Ni-4%CeO_2/Al_2O_3	4:1:0	350	15,000 ml g^{-1} h^{-1}	73.0	98.0	
15%Ni-6%CeO_2/Al_2O_3	4:1:0	350	15,000 ml g^{-1} h^{-1}	67.0	97.0	
15%Ni/SiC	4:1:0	360	12,000 h^{-1}	79	99.6	[7]
15%Ni–5%La/SiC	4:1:0	360	12,000 h^{-1}	85	99.6	
5%Ni/MOF-5	4:1:0	280	2, 000 h^{-1}	16.5	---	[8]
7.5%Ni/MOF-5	4:1:0	280	2, 000 h^{-1}	20.0	---	
10%Ni/MOF-5	4:1:0	280	2, 000 h^{-1}	47.2	---	
12.5%Ni/MOF-5	4:1:0	280	2, 000 h^{-1}	45.1	---	
10%Ni/MOF-5	4:1:0	360	2, 000 h^{-1}	75.1	100	
5%Ni/ $Ce_{0.72}Zr_{0.28}O_2$	4:1:1.1	350	43,000 h^{-1}	71.5	98.5	[9]
10%Ni/ $Ce_{0.72}Zr_{0.28}O_2$	4:1:1.1	350	43,000 h^{-1}	83.4	99.7	
15%Ni/ $Ce_{0.72}Zr_{0.28}O_2$	4:1:1.1	350	43,000 h^{-1}	80.3	99.5	

Catalyst	Molar ratio H_2:CO_2:N_2*	Temp. °C	GHSV	x_{CO2} %	S_{CH4} %	Ref.
$LaNiO_3$ (Act 400°C)	4:1:0	300	7,500 ml g^{-1} h^{-1}	55.4	98.7	[10]
$LaNiO_3$ (Act 500°C)	4:1:0	300	7,500 ml g^{-1} h^{-1}	77.7	99.4	
$LaNiO_3$ (Act 600°C)	4:1:0	300	7,500 ml g^{-1} h^{-1}	71.7	99.3	
$LaNiO_3$ (Act 700°C)	4:1:0	300	7,500 ml g^{-1} h^{-1}	59.7	99.2	
5%Ni/La_2 O_2 CO_3	4:1:0	300	7,500 ml g^{-1} h^{-1}	40.3	88.9	
23%Ni/CaO-Al_2O_3	4:1:3.3	400	15,000 h^{-1}	81	98	[11]
10%Ni/CeO_2	4:1:0	350	10,000 h^{-1}	**92**	100	[12]
10%Ni/MgO	4:1:0	450	10,000 h^{-1}	69	97	
10%Ni/TiO_2	4:1:0	450	10,000 h^{-1}	78	98	
10%Ni/Al_2O_3	4:1:0	450	10,000 h^{-1}	81	99	
(10%Ni-0.1%Ru)/SiC	4:1:1.1	400	10,000 h^{-1}	76.2	98.4	[13]
(10%Ni-0.1%Ru)/$Ce_2Zr_2O_8$	4:1:1.1	400	10,000 h^{-1}	82.2	99.3	
(10%Ni-0.1%Ru)/SiC_{foam}	4:1:1.1	400	10,000 h^{-1}	69.9	93.9	
(2.5%Ni-0.025%Ru)/SiC_{foam}	4:1:1.1	400	10,000 h^{-1}	37.5	76.6	
(2.5%Ni-0.025%Ru)/ (15%CNF-SiC_{foam})	4:1:1.1	400	10,000 h^{-1}	48.6	86.5	
(2.5%Ni-0.025%Ru)/ (1%$Ce_2Zr_2O_8$-SiC_{foam})	4:1:1.1	400	10,000 h^{-1}	46.4	92.3	
(2.5%Ni-0.025%Ru)/ (27%$Ce_2Zr_2O_8$-SiC_{foam})	4:1:1.1	400	10,000 h^{-1}	59.8	96.4	
(2.5%Ni-0.025%Ru)/ (1%$Ce_2Zr_2O_8$-15%CNF-SiC_{foam})	4:1:1.1	400	10,000 h^{-1}	65.1	96.2	
Ni(100)/Al_2 O_3	4:1:0	400	500 mL g^{-1} h^{-1}	17.8	---	[14]
Mn/Ni(40:60)/ Al_2 O_3	4:1:0	400	500 mL g^{-1} h^{-1}	20.1	---	
Mn/Ni(20:80)/ Al_2 O_3	4:1:0	400	500 mLg^{-1} h^{-1}	21.3	---	
Pd/Mn/Ni(5:35:60)/Al_2 O_3	4:1:0	400	500 mL g^{-1} h^{-1}	21.0	---	
Ru/Mn/Ni(5:35:60)/Al_2 O_3	4:1:0	400	500 mL g^{-1} h^{-1}	**99.7**	72.36	
Pd/Mn/Ni(5:15:80)/ Al_2 O_3	4:1:0	400	500 mL g^{-1} h^{-1}	13.0	---	
Ru/Mn/Ni(5:15:80)/ Al_2 O_3	4:1:0	400	500 mL g^{-1} h^{-1}	51.0	---	
5%Ni/Zr/CNT-SEQ	5:1:94	400	75,000 mL g^{-1} h^{-1}	55	98	[17]
5%Ni/CNT	5:1:94	450	75,000 mL g^{-1} h^{-1}	48	30	
5%Ni/Zr/CNT-COI	5:1:94	500	75,000 mL g^{-1} h^{-1}	47	12	
15%Ni/ZrO_2	4:1:0.55	300	48,000 mL g^{-1} h^{-1}	60	98	[18]
40Ni-$Ce_{0.9}Zr_{0.1}O$	4:1:0	275	3,000 mL g^{-1} h^{-1}	**98**	100	[19]
15%Ni/ZrO_2-O	4:1:0.55	400	50,000 mL g^{-1} h^{-1}	80	100	[20]
15%Ni/ZrO_2	4:1:0.55	400	50,000 mL g^{-1} h^{-1}	75	100	

Catalyst	Molar ratio $H_2:CO_2:N_2$*	Temp. °C	GHSV	x_{CO_2} %	S_{CH_4} %	Ref.
20%Ni/ZrO2-COP	4:1:5	400	126, 000 mL g^{-1} h^{-1}	55	100	This work
20%Ni/ZrO2-COP	4:1:5	400	43, 500 mL g^{-1} h^{-1}	50	100	This work

* Molar ratio for H_2 and N_2 are calculated on CO_2 mole basis.

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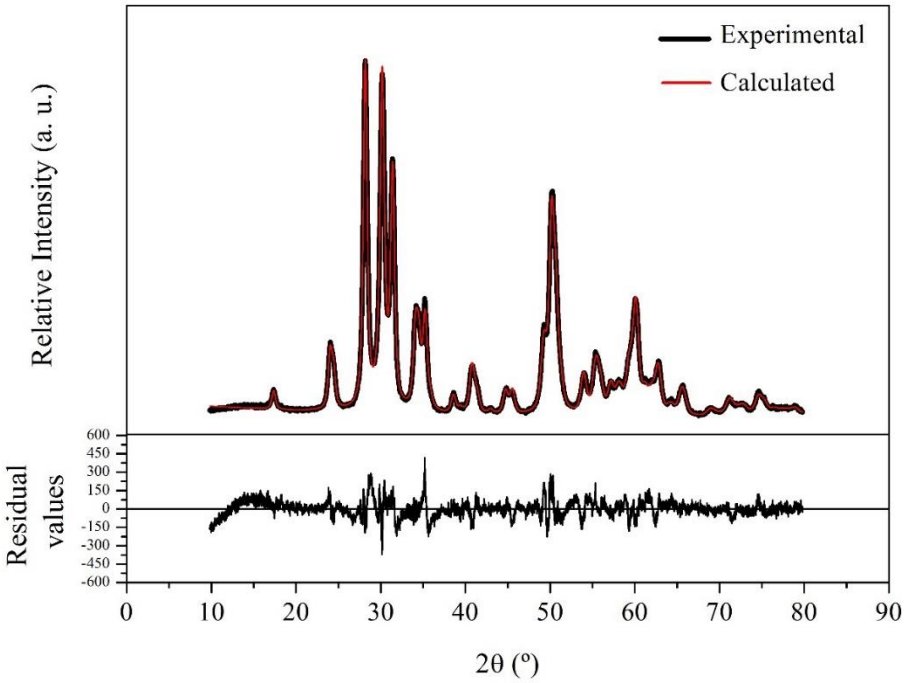

Figure S1. Rietveld simulation for the sol-gel ZrO_2 support.

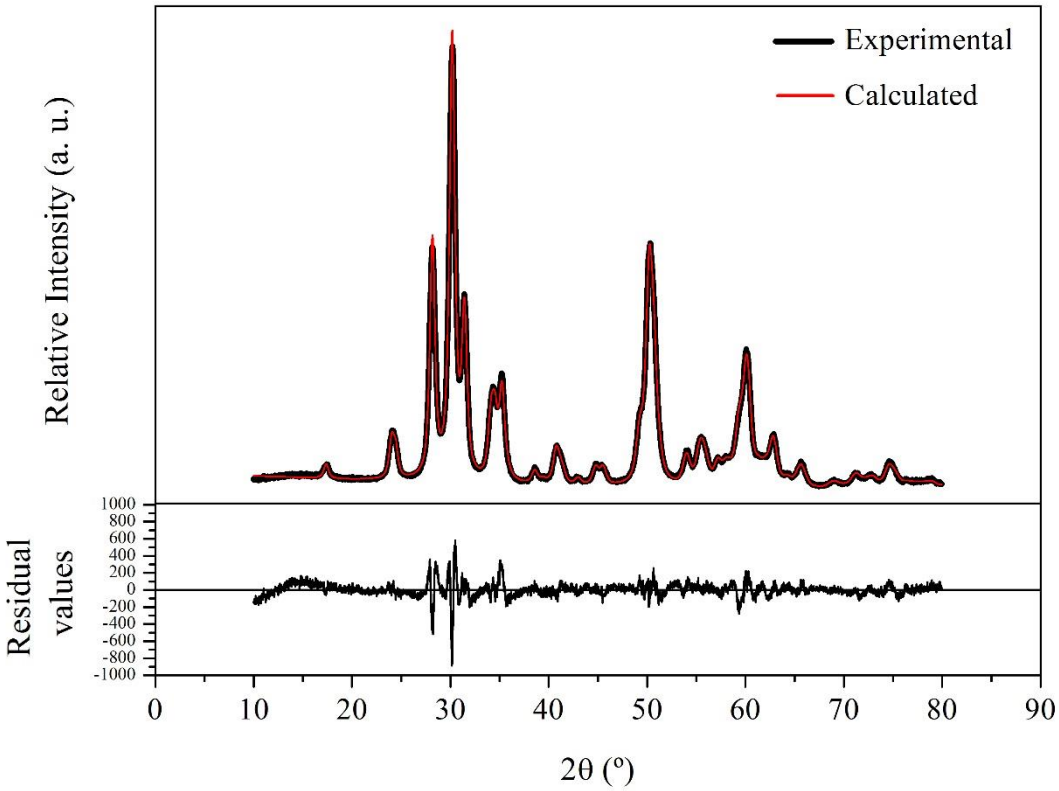

Figure S2. Rietveld simulation for the co-precipitation ZrO_2 support.

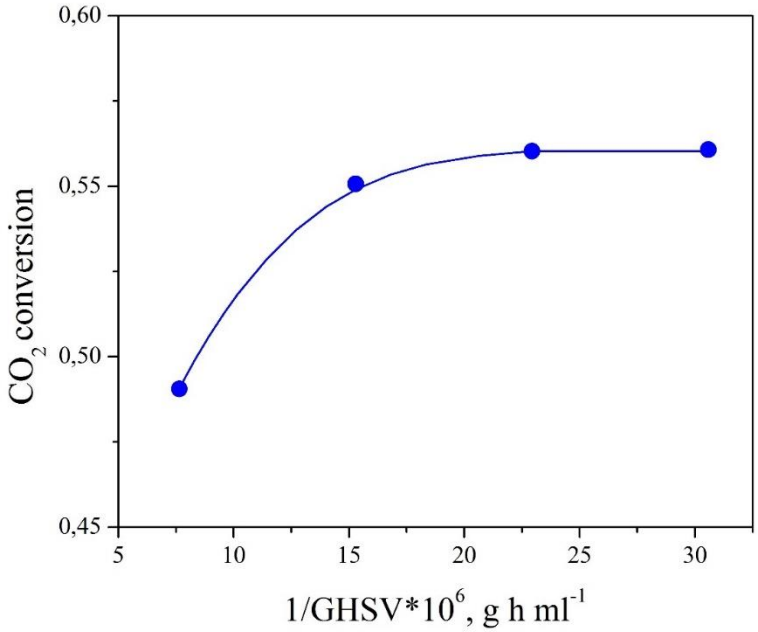

Figure S3. Effect on GHSV on CO_2 conversion with the 20%Ni/$ZrO_{2\text{-}COP}$ catalyst. Reaction conditions: 400 ºC, 0.1 MPa.

20%Ni/ZrO2-COP (Fresh) 20%Ni/ZrO2-COP (Spent)

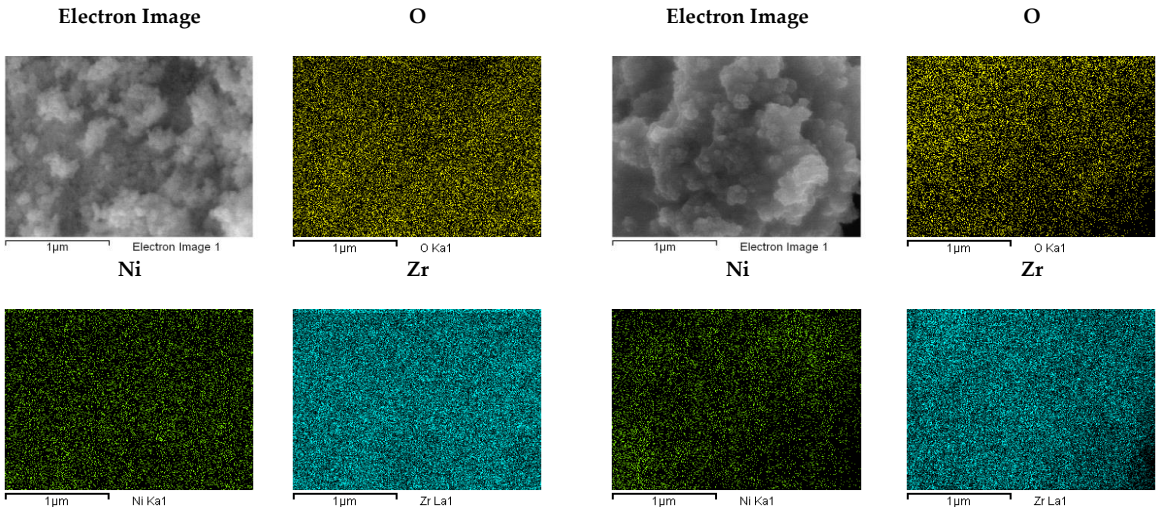

Figure S4. SEM images of 20%Ni/$ZrO_{2\text{-}COP}$ catalysts.

Table S2. SEM microanalysis.

wt%	Catalyst	
	20%Ni/ZrO$_{2\text{-COP-F}}$	**20%Ni/ZrO$_{2\text{-COP-S}}$**
O	28.6	28.1
Ni	18.4	20.2
Zr	53.0	51.6

Catalyst dispersion calculations

Table S3. Peak areas of the hydrogen chemisorption analysis.

Injection #	Peak Area 20%Ni/ZrO2-COP Fresh catalyst *m*=0.052 g	Peak Area 20%Ni/ZrO2-COP Spent catalyst *m*=0.012 g
1	7.34	144.62
2	17.74	154.02
3	28.40	154.15
4	41.00	157.43
5	59.08	158.50
6	80.74	160.49
7	112.86	162.19
8	114.92	166.47
9	113.47	161.75
10	121.85	161.90
11	121.40	163.67
12	125.05	165.25
13	129.51	165.54
14	131.09	164.49
15	132.01	167.61

$$\%D = \left[n\left(\frac{V_{ads}}{V_g}\right)\left(\frac{MW}{M}\right)100\right]100$$

$\%D$ = metal dispersion, %.

n =stoichiometry factor = 2

V_{ads} = volume of the active gas adsorbed, cm^3/g

V_g = molar volume gas at STP = 22414 cm^3/mol

MW = molecular weight of nickel=58.693 g/mol

M = % of metal loading = 20%

$$V_{ads}(STP) = \frac{V_{inj}}{m}\sum_{i=1}^{n}\left(1 - \frac{Ai}{Af}\right)$$

m = mas of the sample, g

A_i = Area of the peak i

A_f = area of the last peak

$$V_{inj}(STP) = V_{loop}\left(\frac{T_{std}}{T_{room}}\right)\left(\frac{P_{room}}{T_{std}}\right)\left(\frac{A}{100}\right)$$

V_{inj} = Volume of the active gas injected, cm^3

V_{loop} =Volume of the loop, cm^3

T_{room} = room temperature, K

P_{room} = room pressure, mmHg

T_{std} = standar temperature= 273.15 K

P_{std} = standard pressure= 760 mmHg

A = % of active gas in the gas-mixture