catalysts

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Article

The effect of CeO_2 preparation method on the carbon pathways in dry reforming of methane on 5 wt% Ni/CeO_2 studied by transient techniques

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2. Results

2.1. Catalysts surface texture and structural properties

Table S1. Textural and structural characterization of 5 wt% Ni/CeO_2 (-TD, -PT, -HT and -SG) DRM fresh catalysts.

Catalyst (5 wt% Ni)	SSA ($m^2\ g^{-1}$)	V_P ($cm^3\ g^{-1}$)	d_P (nm)	d_C (nm)	a (Å)	d_{Ni} (nm)	D_{Ni} (%)
CeO_2-TD	23	0.102	17.7	19.6[a]	5.4088[a]	11.0[b]	8.8[b]
						12.4[c]	7.8[c]
CeO_2-PT	5.6	0.032	22.5	29.9[a]	5.4091[a]	13.6[b]	7.1[b]
						15.9[c]	6.1[c]
CeO_2-HT	50	0.203	15.8	11.5[a]	5.4104[a]	8.4[b]	11.5[b]
						10.1[c]	9.6[c]
CeO_2-SG	14.5	0.029	6.7	43.1[a]	5.3988[a]	20.8[b]	4.7[b]
						28.5[c]	3.4[c]

[a] estimated based on the 2θ=28.7° diffraction peak of CeO_2 (111) face; [b] estimated based on the 2θ=37.2° diffraction peak of NiO (111) face and after considering the mass densities of Ni^0 and NiO phases; [c] estimated from TPD studies.

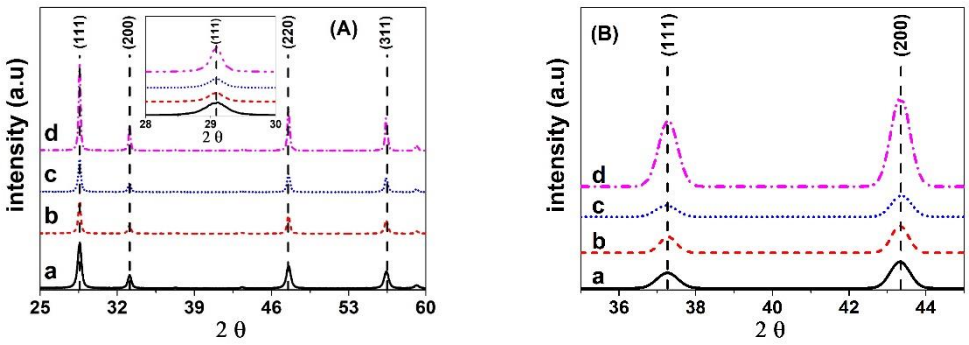

Figure S1. Powder X-ray diffractograms of 5 wt% Ni supported on (a) CeO_2-TD, (b) CeO_2-PT, (c) CeO_2-HT and (d) CeO_2-SG carriers in the (A) 20-70° 2θ and (B) 35-45° 2θ region (diffraction peaks of NiO).

2.2. Transmission Electron Microscopy (TEM) studies

Representative HR-TEM micrographs include structural and morphological information about the fresh 5 wt% Ni supported on CeO_2 prepared by the hydrothermal (HT) method (Figs. S2). The 50 nm resolved image shows that the support consists of agglomerated polyhedral primary crystallites (10-20 nm) of CeO_2. In addition, Fig. S2 image resolved at 10 nm, clearly shows NiO particles in the 8-12 nm range. The latter results correspond closely with the PXRD and H_2-TPD studies reported in Results section and Table S1.

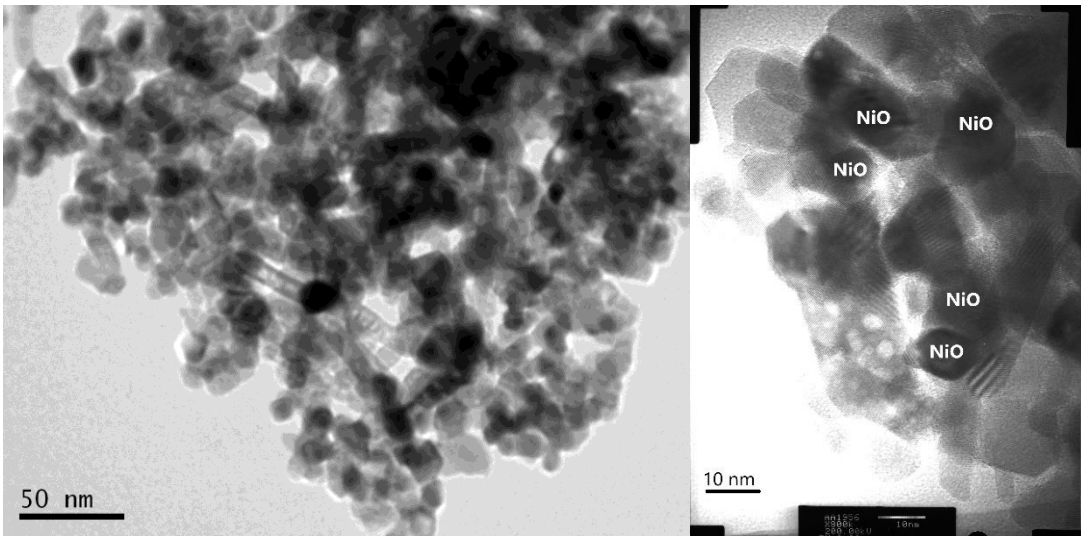

Figure S2. Representative HR-TEM images of the calcined (air, 750 °C/4 h) 5 wt% Ni/CeO_2-HT catalyst. Left graph: magnification at 50 nm unit scale; Right graph: magnification at 10 nm unit scale.

2.3. Scanning Electron Microscopy (SEM) studies

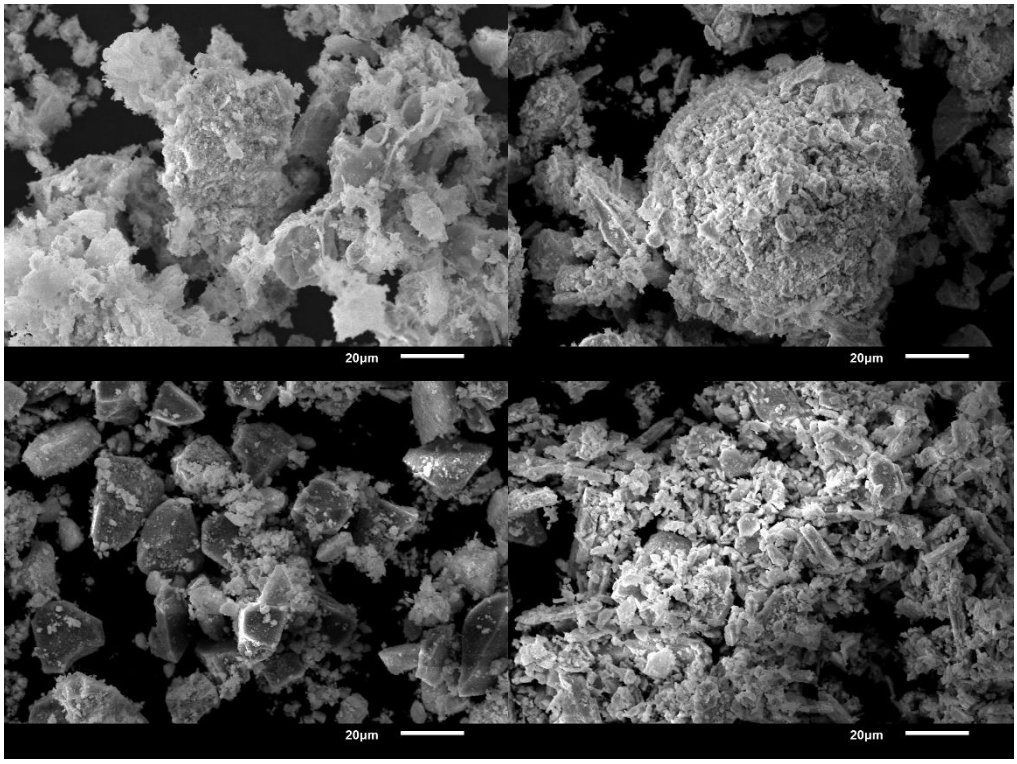

Figure S3. SEM images of the fresh Ni/CeO_2-SG (top left), Ni/CeO_2-PT (top right), Ni/CeO_2-HT (down left) and Ni/CeO_2-TD (down right).

2.4. Catalytic performance studies during DRM

Table S2. Catalytic activity in terms of CH_4, CO_2 conversion (X_{CH4}, X_{CO2}, %), H_2 Yield (%) and H_2/CO gas product ratio obtained after 30 min in DRM at 750 °C for the four ceria supports prepared by different methods.

Catalyst (5 wt% Ni)	X_{CH4} (%)	X_{CO2} (%)	H_2 Yield (%)	H_2/CO
CeO_2-TD	87.5	87.4	58.4	1.2
CeO_2-PT	89.8	89.5	51.4	1.2
CeO_2-HT	93.2	91	55.3	1.2
CeO_2-SG	81.2	90.3	48.6	1.1

Table S3. Catalytic stability performance in terms of CH_4, CO_2 conversion (X_{CH4}, X_{CO2}, %), H_2 Yield (%), H_2/CO gas product ratio and carbon deposition (mg C g^{-1}_{cat}) obtained during DRM (20% CH_4/20% CO_2/He) at 750 °C over the 5 wt% Ni/CeO_2-PT solid.

TOS (h)	X_{CH4} (%)	X_{CO2} (%)	H_2 Yield (%)	H_2/CO	C deposition (mg C g^{-1}_{cat})
0.5	89.8	89.5	51.4	1.2	-
1	89.4	88.6	51.2	1.2	-
2	89.2	88.2	50.8	1.2	-
6	89.1	88.0	50.8	1.2	-
12	87.9	87.7	50.4	1.2	30.7
24	75.2	84.6	50.0	1.2	-
36	74.6	84.1	47.6	1.1	-
50	74.1	83.0	45.4	1.1	147.1

Table S4. Catalytic activity in terms of CH_4, CO_2 conversion (X_{CH4}, X_{CO2}, %), H_2 Yield (%) and H_2/CO gas product ratio obtained after 30 min in DRM (5 vol% $^{13}CO_2$/5 vol% $^{12}CH_4$/He) at 750 ^{o}C.

Catalyst 5 wt% Ni	X_{CH4} (%)	X_{CO2} (%)	H_2 Yield (%)	H_2/CO
CeO_2-TD	97.9	91.3	97.6	1.1
CeO_2-PT	98.5	91.6	95.6	1.1
CeO_2-HT	98.5	92.0	99.4	1.1
CeO_2-SG	95.0	92.0	79.1	1.0

2.5. Characterization of carbon formed under different reaction conditions

Table S5. Carbon accumulation (mg C g_{cat}^{-1}) estimated via TPO followed individual reactions over all catalysts at 750 ^{o}C; 20 vol% CO_2/20 vol% CH_4/He (12h), 5 vol% $^{13}CO_2$/5 vol% $^{12}CH_4$/He (30 min), 20 vol% CH_4/He (30min), 20 vol% CO/He (30 min), 2.5 vol% ^{13}CO/2.5 vol% $^{12}CH_4$/He (20 min).

Catalyst (5 wt% Ni)	DRM (12 h)	$^{13}CO_2/^{12}CH_4$ (30 min)	CH_4 decomp. (30 min)	CO dissoc. (30 min)	$^{13}CO/^{12}CH_4$ (20 min)
CeO_2-TD	66.2	0.13	145.1	13.7	67.2
CeO_2-PT	30.7	-	99.5	32.2	63.5
CeO_2-HT	115.1	0.35	81.1	9.2	103.4
CeO_2-SG	80.4	0.34	128.3	7.7	78

2.6. Participation of support's lattice oxygen under DRM conditions

Table S6. ^{18}O consumption (mmol g^{-1}) during $^{16}O/^{18}O$ exchange, $C^{18}O$ formation (mmol g^{-1}) during DRM following $^{16}O/^{18}O$ oxygen exchange, and $C^{18}O/^{18}O$ ratio.

Catalyst (5 wt% Ni)	^{18}O consumption (mmol g^{-1})	$C^{18}O$ production (mmol g^{-1})	$C^{18}O/^{18}O$
CeO_2-TD	12.4	5.9	0.48
CeO_2-PT	11	3.5	0.31
CeO_2-HT	11.4	6.5	0.57
CeO_2-SG	10.2	3.3	0.32