

Supplemental Information

Investigation of Titania and Ceria Support Effects in Nickel Catalyzed CO₂ Methanation

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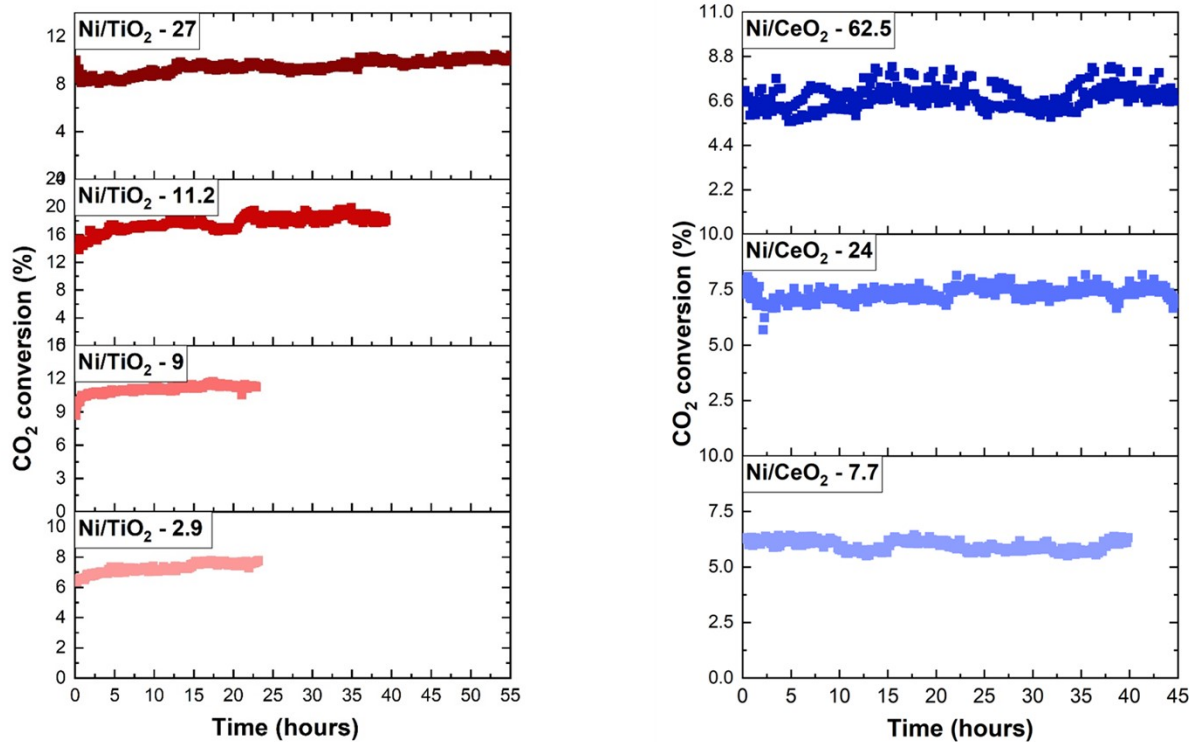


Figure S1. Stability plots of Ni-based catalysts studied in this work.

Table S1. Reactivity data of the catalysts studied in this work.

Catalyst	Total flow rate (sccm)	Average CO ₂ conversion (%) ^a	Average CH ₄ Production (μmol/min/g Ni) ^{a,b}	Stable time range used to calculate average CO ₂ conversion and CH ₄ production (hrs.) ^a
Ni/TiO ₂ -2.9	100	7.2±0.1	7779	8-13 hrs.
Ni/TiO ₂ -9	200	11.1±0.1	13524	10-15 hrs.
Ni/TiO ₂ -11.2	400	18.2±0.4	48105	23-28 hrs.
Ni/TiO ₂ -27	100	10.1±0.1	7350	50-55 hrs.
Ni/CeO ₂ -7.7	100	5.8±0.1	9146	25-30 hrs.
Ni/CeO ₂ -24	100	7.6±0.2	6370	21-26 hrs.
Ni/CeO ₂ -62.5	50	7±0.4	2348	40-45 hrs.

^a Reaction conditions: 300 °C, 1 atm, CO₂:H₂:N₂ = 1:4:5. The reported CO₂ conversion and CH₄ production were calculated at the steady state activity after the activation period. ^b Average CH₄ production is based on ICP Ni loading.

Table S2. Comparison of the reported materials against existing literature

Catalyst	Ni particle size (nm)	Reaction Temperature (°C) and Pressure (atm)	Maximum CH ₄ selectivity (%)	TOF (s ⁻¹)	Reference
Ni/TiO ₂	2.9-27	300 °C, 1 atm	100	0.02-0.53	Studied in this work
Ni/CeO ₂	7.7-62.5	300 °C, 1 atm	100	0.07-0.15	Studied in this work
Ni/CeO ₂	2-8	300 °C, 1 atm	91	0.001-0.06	⁴⁸
Ni/Al ₂ O ₃	11.41-16.98	400 °C, 1 atm	50	1.32-2.02	⁵⁹
Ni/Al ₂ O ₃	8.5	250 °C, 1 atm	32	0.007	⁶⁰
Ni/SiO ₂	3.5-7.5	250 °C, 1 atm	93	0.001-0.004	⁶¹
Ni/SiO ₂	1.1-6.9	300 °C, 4.9 atm	99.5	0.01-0.07	⁴⁴
Ni/SiO ₂	2.7-12.2	220 °C, 1 atm	90	0.001-0.002	⁶²

Absence of transport limitations:

We calculate the Weisz-Prater (W-P) criterion to confirm the absence of transport limitations.¹ The Weisz-Prater Criterion is defined as

$$N_{W-P} = \frac{R_p^2 r_{obs}}{D_{eff} C_S}$$

Where r_{obs} is the rate per catalyst volume, R_p is the radius of the catalyst particle, C_S is the concentration of reactants (CO_2 and H_2) at the catalyst surface, and D_{eff} is the effective diffusivity considered for both CO_2 and H_2 molecule separately.

The parameters used in the case of the catalyst studied in this work are provided in Table S2 and the W-P criteria for all catalysts are shown in Table S3.

Table S3. Parameters used in calculation of the W-P criterion.

Parameter	Value
Catalyst particle radius (R_p) (cm) ^a	0.021
Specific reactor volume (V_s) ($cm^3 g_{cat}^{-1}$)	3.68
Average velocity for the CO_2 molecules (\bar{v}) ($cm s^{-1}$)	5.25×10^4
Mean free path (λ) (cm) for CO_2 molecule	5.07×10^{-5}
Molecular diameter of CO_2 (σ) (cm)	3.3×10^{-8}
Average velocity for the H_2 molecules (\bar{v}) ($cm s^{-1}$)	2.5×10^5
Mean free path (λ) (cm) for H_2 molecule	3.1×10^{-5}
Molecular diameter of H_2 (σ) (cm)	2.4×10^{-8}
Reaction Temperature (T)(K)	573
Gas constant (R) ($atm cm^3 g_{mole}^{-1} K$)	82.06
Boltzmann constant (k_B) ($erg K^{-1}$)	1.38×10^{-16}

^a For all catalysts, the particles passed through a 40-mesh screen, which represents a 0.042 cm opening and a maximum radius of $R_p=0.021$ cm.

Table S4. W-P Criterion for the catalysts studied in this work.

Catalyst	r^{obs} (mol/s/gcm ³)	N_{W-P} for CO ₂	N_{W-P} for H ₂
Ni/TiO ₂ -2.9	5.57×10^{-7}	2.64×10^{-3}	1.39×10^{-4}
Ni/TiO ₂ -9	1.63×10^{-6}	7.71×10^{-3}	4.06×10^{-4}
Ni/TiO ₂ -11.2	5.82×10^{-6}	2.75×10^{-2}	1.45×10^{-3}
Ni/TiO ₂ -27	8.19×10^{-7}	3.88×10^{-3}	2.04×10^{-4}
Ni/CeO ₂ -7.7	4.27×10^{-7}	5.05×10^{-3}	2.66×10^{-4}
Ni/CeO ₂ -24	6.09×10^{-7}	7.21×10^{-3}	3.79×10^{-4}
Ni/CeO ₂ -62.5	2.94×10^{-7}	3.48×10^{-3}	1.83×10^{-4}

The Weisz-Prater number, N_{W-P} (for CO₂ and H₂ separately) indicates negligible diffusional limitations when $N_{W-P} \leq 0.3$. All reactions conducted in this work are not limited by transport effects.

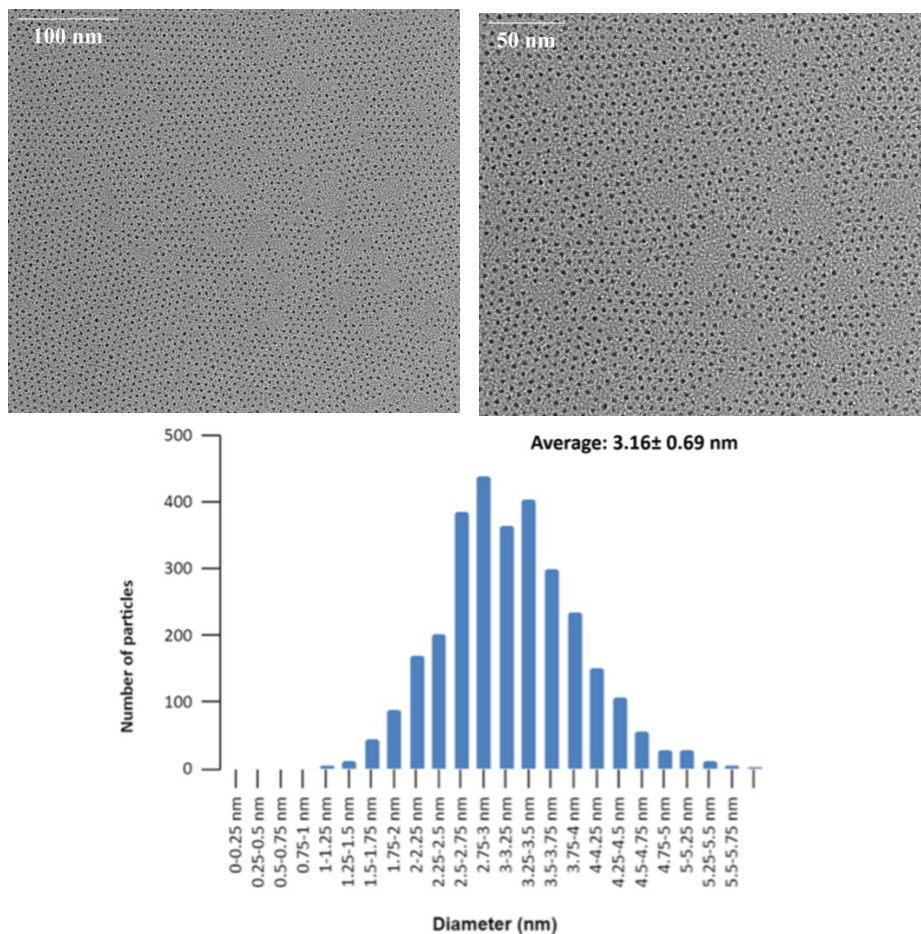


Figure S2. TEM images of the colloidal nickel nanoparticles in solution, and the corresponding particle size distribution. We note that all supported colloidal catalysts were prepared from this same batch of Ni nanoparticles.

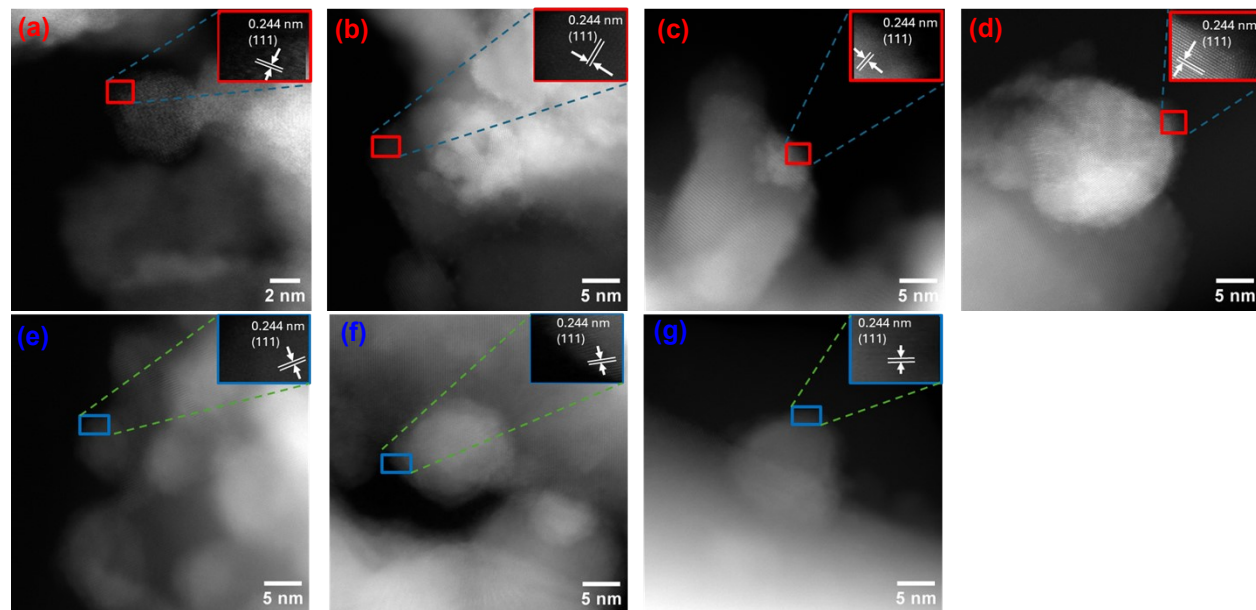


Figure S3. Absence of SMSI of the catalysts studied in this work. a) Ni/TiO₂ - 2.9, b) Ni/TiO₂ -9, c) Ni/TiO₂ - 11.2, d) Ni/TiO₂ - 27, e) Ni/CeO₂ - 7.7, e) Ni/CeO₂ - 24, f) Ni/CeO₂ - 62.5. The boxes (red for Ni/TiO₂ and blue for Ni/CeO₂) indicate the region where the possibilities of formation of SMSI layer. (d spacing for NiO (111) is 0.244 nm.)

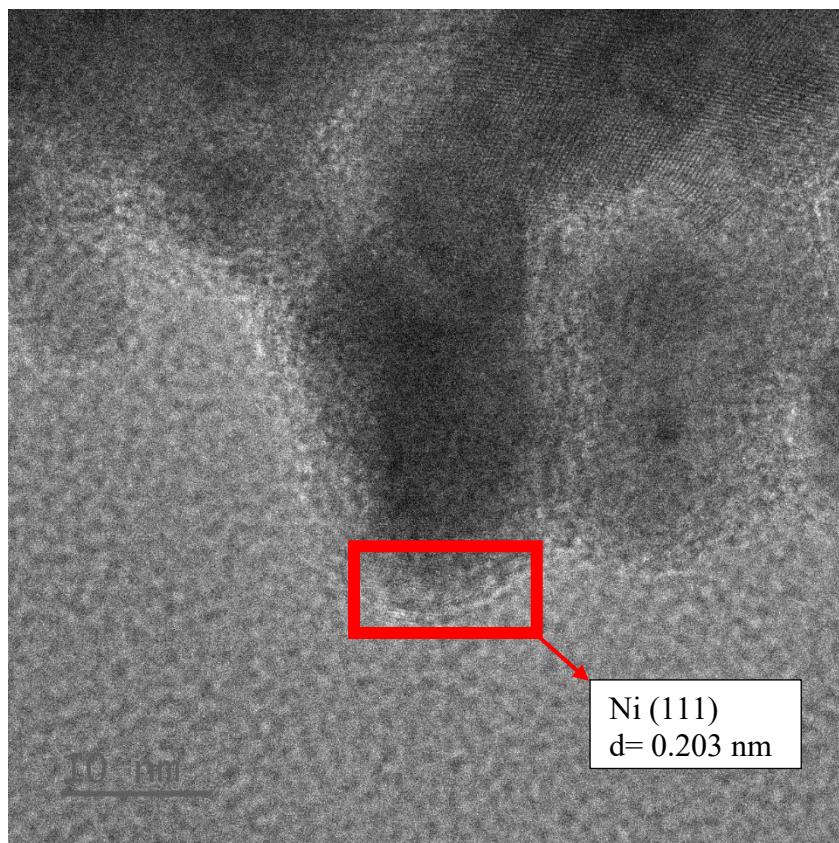


Figure S4. TEM image of the Ni/CeO₂-7.7 catalyst.

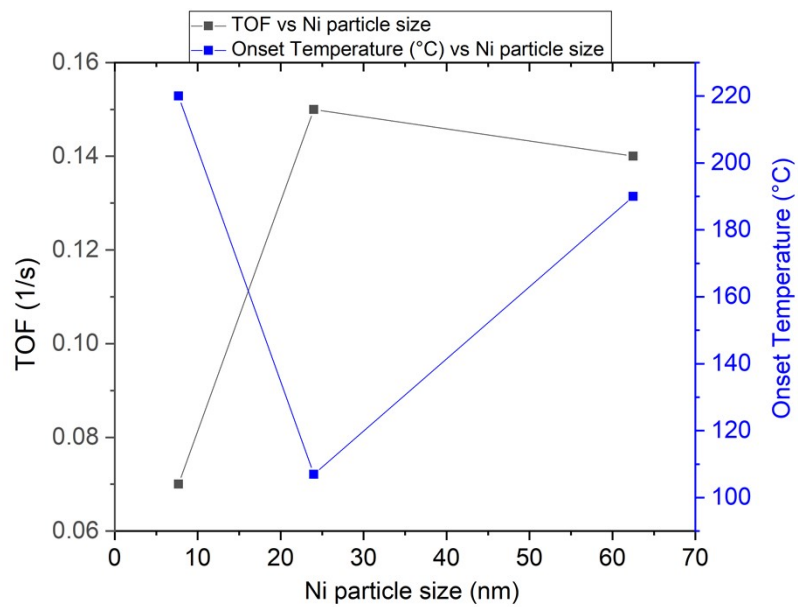


Figure S5. Onset temperature of reduction for Ni/CeO₂ catalysts.

AgO calibration

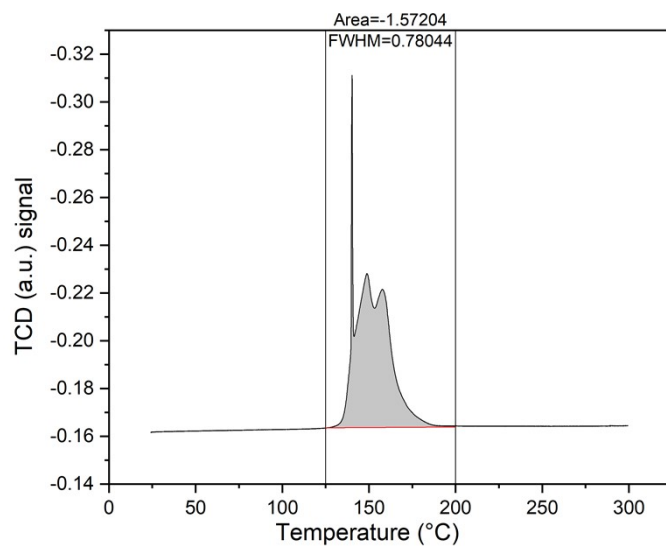
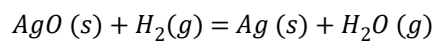


Figure S6. Standard AgO calibration H₂-TPR.

Calculation of standard AgO calibration



$$1 \text{ g AgO} \equiv 96.7 \text{ cm}^3 \text{ H}_2 \text{ (STP)}$$

We used 0.0395 g AgO in the calibration:

$$0.0395 \text{ g AgO} \equiv 3.818 \text{ cm}^3 \text{ H}_2$$

According to the experiment, 0.0395 g AgO \equiv 1.57 TCD (a.u.) * °C area
so, 1.57 TCD (a.u.) * °C area \equiv 3.818 cm³ H₂

Table S5. H₂ consumption on pristine supports and Ni catalysts as determined by H₂ TPR and AgO calibration for Ni/TiO₂ (top) and Ni/CeO₂ (bottom).

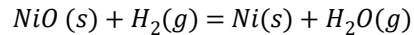
Ni/TiO₂ catalysts

Catalyst	Area (80-650 °C) (a.u.* °C/ g of material)	Area (80-650 °C) (a.u.* °C/ g of material)	Reduction range (80-650 °C) (H ₂ consumed cm ³ / g of material)	Reduction range (650-900 °C) (H ₂ consumed cm ³ / g of material)	Total H ₂ consumption (H ₂ consumed cm ³ / g of material)
TiO ₂	1.14	3.36	2.78	8.17	10.95
Ni/TiO ₂ - 2.9	7.81	0.92	18.98	2.24	21.22
Ni/TiO ₂ - 9	4.91	0.19	12.41	2.8	15.21
Ni/TiO ₂ - 11.2	7.02	2.87	17.07	6.98	24.05
Ni/TiO ₂ - 27	4.06	1.33	9.87	3.24	13.11
Ni/TiO ₂ SEA Unreduced	14.81	1.57	35.99	3.84	39.74

Ni/CeO₂ catalysts

Catalyst	Area (100-550 °C) (a.u.* °C/ g of material)	Area (550-900 °C) (a.u.* °C/ g of material)	Reduction range (100-550 °C) (H ₂ consumed cm ³ / g of material)	Bulk CeO ₂ reduction (550-900°C) (H ₂ consumed cm ³ / g of material)	Total H ₂ consumption (H ₂ consumed cm ³ / g of material)
CeO ₂	-	11	-	26.73	26.73
Ni/CeO ₂ -7.7	1.11	8.30	2.69	20.17	22.86
Ni/CeO ₂ - 24	1.23	9.74	2.99	23.67	26.66
Ni/CeO ₂ - 62.5	1.10	9.09	2.67	22.08	24.75
Ni/CeO ₂ SEA Unreduced	6.27	10.57	15.23	25.66	40.89
Ni/CeO ₂ IWI Unreduced	11.12	8.96	27.03	21.77	48.8

Theoretical calculations for H₂ consumption during NiO reduction.



$$74.69 \text{ g NiO} = 22400 \text{ cm}^3 \text{H}_2$$

$$3 \text{ wt.}\% \text{ Ni} \equiv 0.0377 \frac{\text{g Ni}^{2+}}{\text{g of catalyst}}$$

$$\begin{aligned} \text{H}_2 \text{ needed for all NiO reduction} &= \frac{22400 \times 0.0377}{74.69} \frac{\text{cm}^3 \text{H}_2}{\text{g of catalyst}} \\ &= 11.3 \frac{\text{cm}^3 \text{H}_2}{\text{g of catalyst}} \end{aligned}$$

Table S6. Distribution of basic sites on pristine supports and Ni catalysts determined by CO₂ TPD^a

Materials	Weak + Medium basic sites area ^a	Strong basic sites area ^a	Total area	Weak + Medium basic sites (%)	Strong basic sites (%)
TiO₂	10.15	1.65	11.8	86	14
Ni/TiO₂ - 2.9	8.10	1.26	9.36	86.5	13.5
Ni/TiO₂ - 9	7.31	1.83	9.14	80	20
Ni/TiO₂ - 11.2	9.63	3.06	12.69	75.9	24.1
Ni/TiO₂ - 27	0.99	1.71	2.7	36.7	63.3
Only CeO₂	1.12	0.61	1.73	64.7	35.3
Ni/CeO₂ - 7.7	0.35	0.11	0.46	76	24
Ni/CeO₂ - 24	0.39	0.37	0.76	51.3	48.7
Ni/CeO₂ - 62.5	0.47	0.83	1.3	36.2	63.8

^a These basic site fractions were calculated from the peak area defined by 100-450 °C, and 450-900 °C, corresponding to the weak + medium, and strong basic sites, respectively, using a baseline of Y axis offset of left and right for each catalyst.

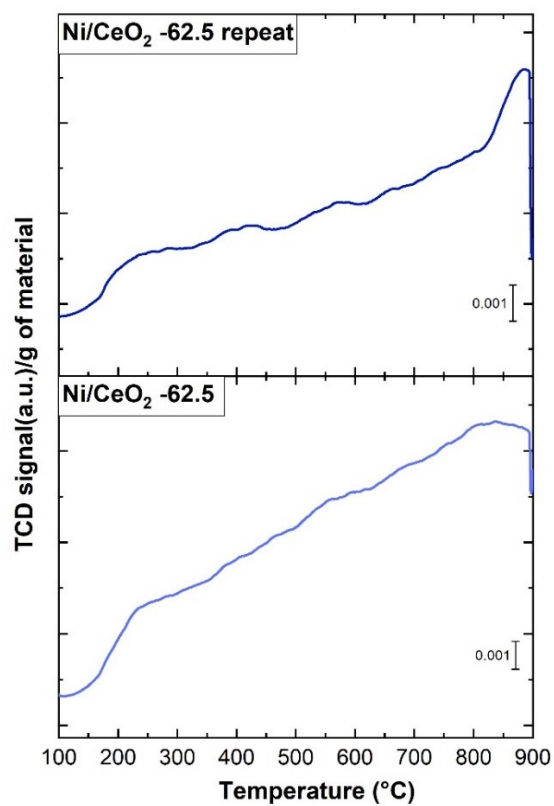


Figure S7. CO₂-TPD repeat on Ni/CeO₂ -62.5

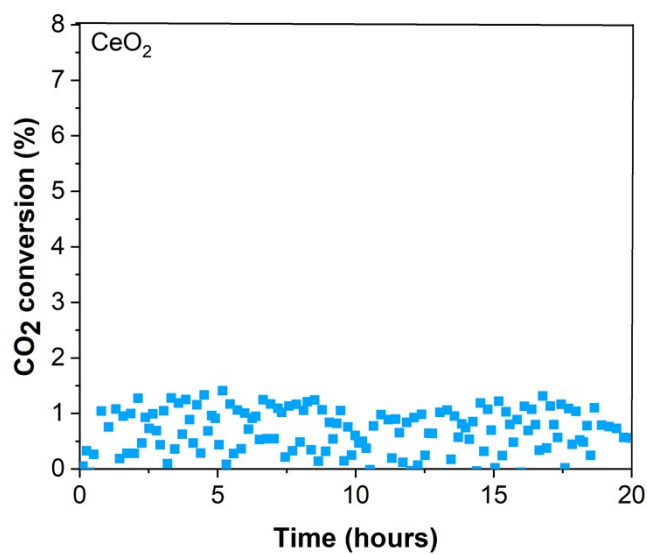


Figure S8. Reaction on CeO₂ only at 50 sccm and 300 °C. Pristine CeO₂ has a reactivity of 7 μmol/min/g of CeO₂ between 5 and 10 hrs.

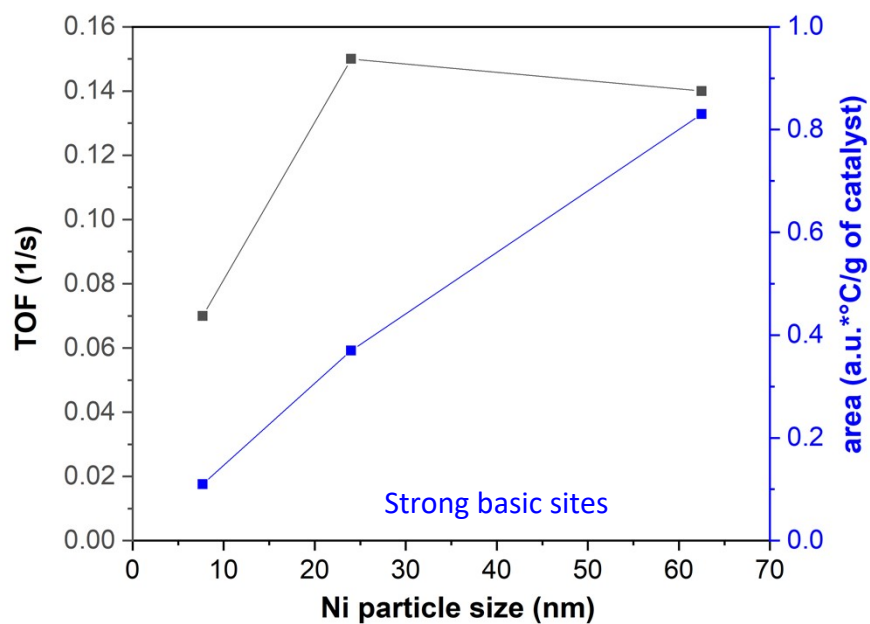


Figure S9. The CO₂ methanation turnover frequency (black) and area of strong basic sites (blue) from temperature programmed desorption on Ni/CeO₂ as a function of Ni particle size for the catalysts studied in this work.

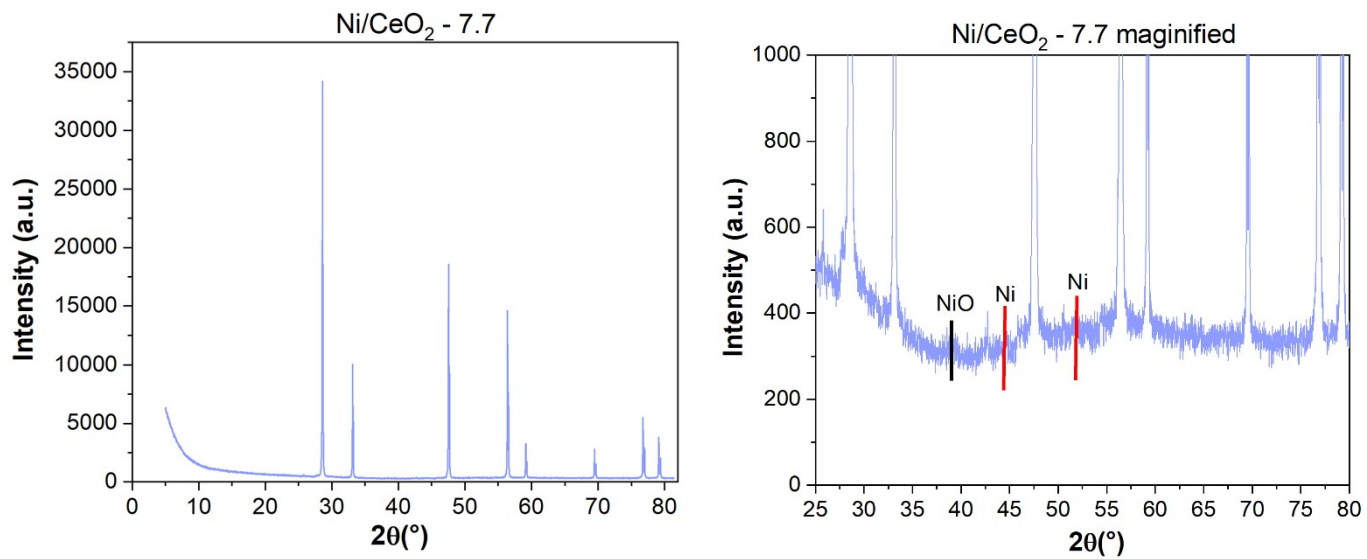
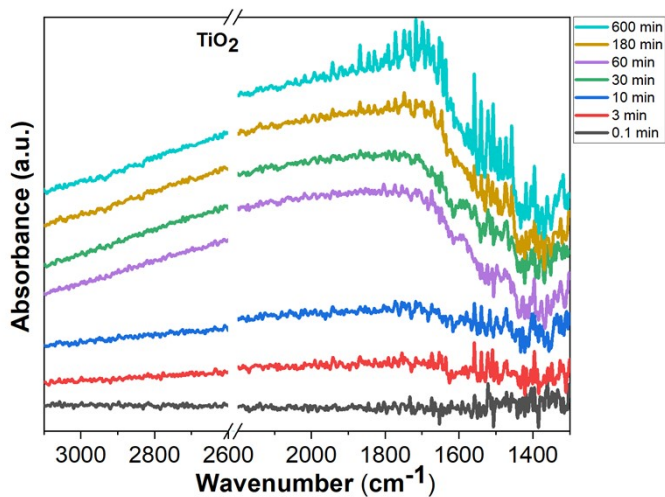
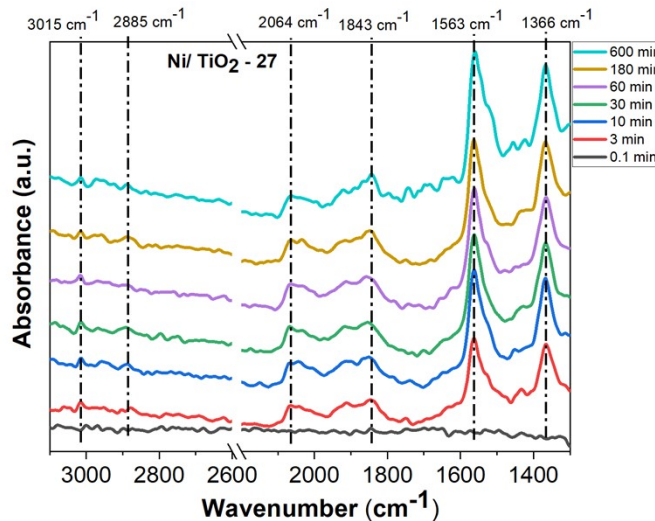
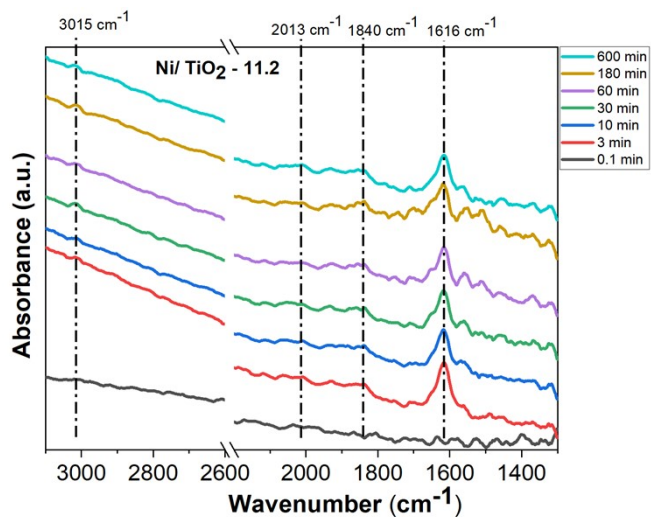
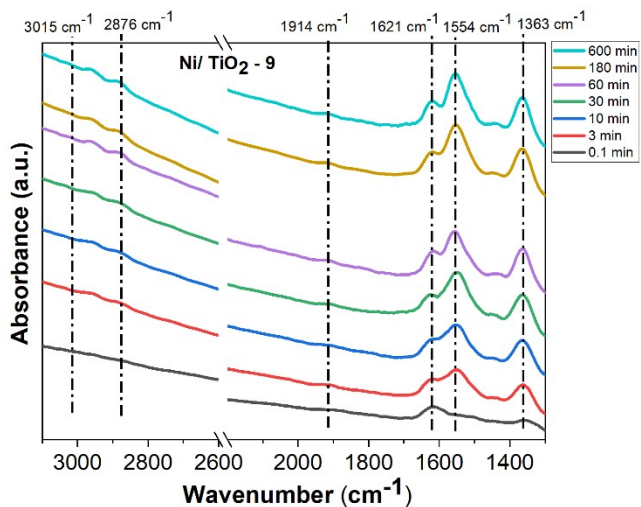
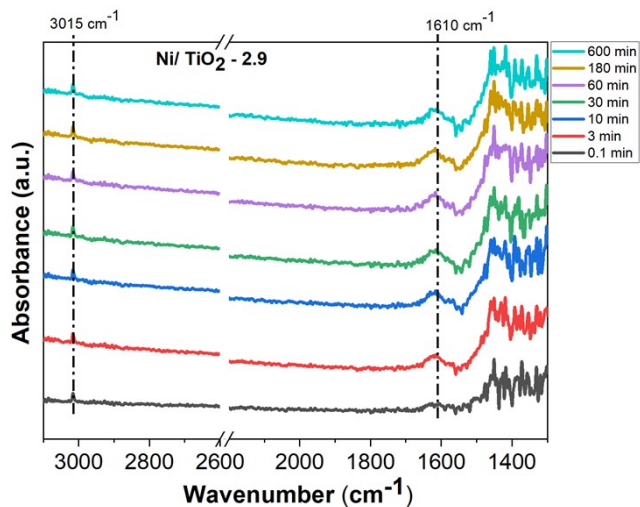


Figure S10. XRD patterns of the Ni/CeO₂-7.7 catalyst.



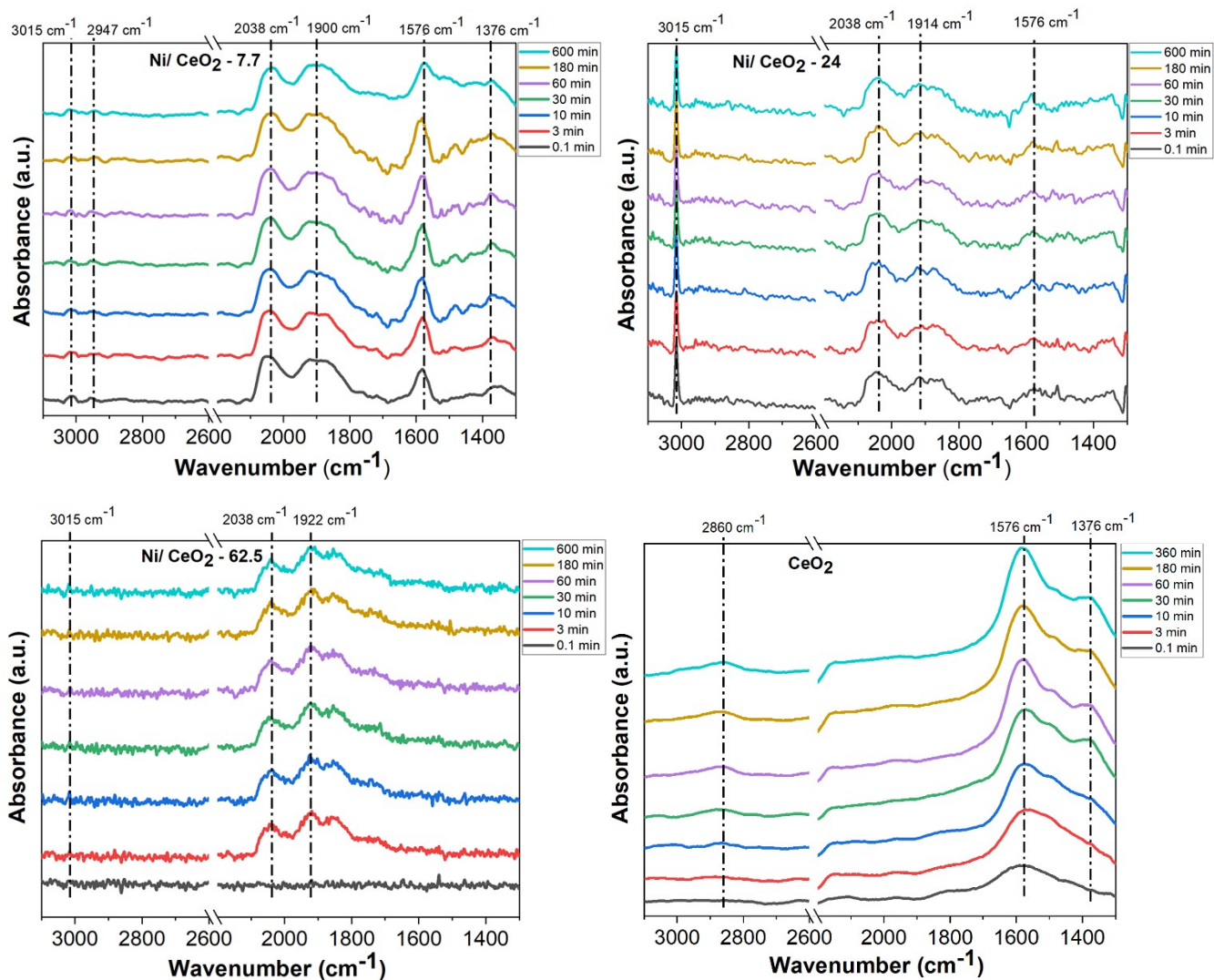


Figure S11. Time lapse *in situ* FTIR on the catalysts and CeO₂ support studied in this work. All catalysts were reduced *in situ* at 477 °C for 2 hrs prior to switching to the CO₂, H₂, Ar mixture at 300° C. The spectra shown were collected after 10 hrs. of reaction and a background of the reduced catalysts under H₂/Ar flow is subtracted.

Reference

- (1) Vannice, M. A. *Kinetics of Catalytic Reactions*; Springer US: Boston, MA, 2005.
<https://doi.org/10.1007/b136380>.