

Electronic Supplementary Material

Characterization and catalytic activity of soft-templated NiO-CeO₂ mixed oxides for CO and CO₂ co-methanation

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X-ray diffraction (XRD)

X-ray diffraction (XRD) patterns were collected using an X3000 diffractometer (Seifert) with θ - θ Bragg-Brentano geometry with Cu-K α wavelength and a graphite monochromator before the detector. The average crystallite sizes were estimated by the Scherrer equation.

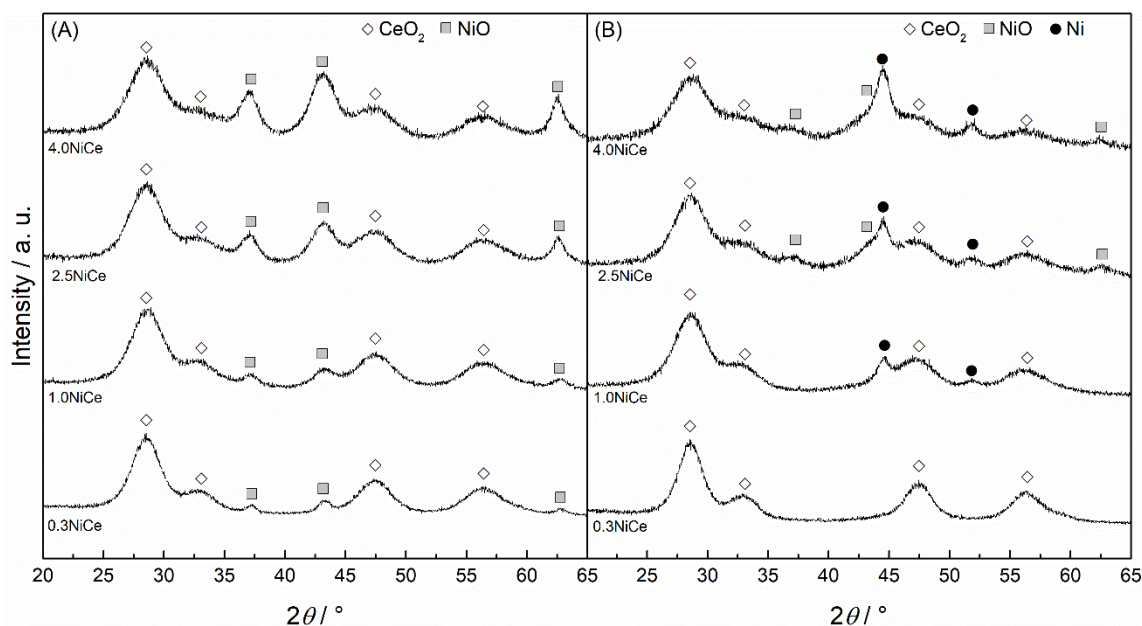


Figure S1. XRD patterns of the xNiCe samples before (A) and after (B) the H₂-pretreatment.

Transmission Electron Microscopy (TEM)

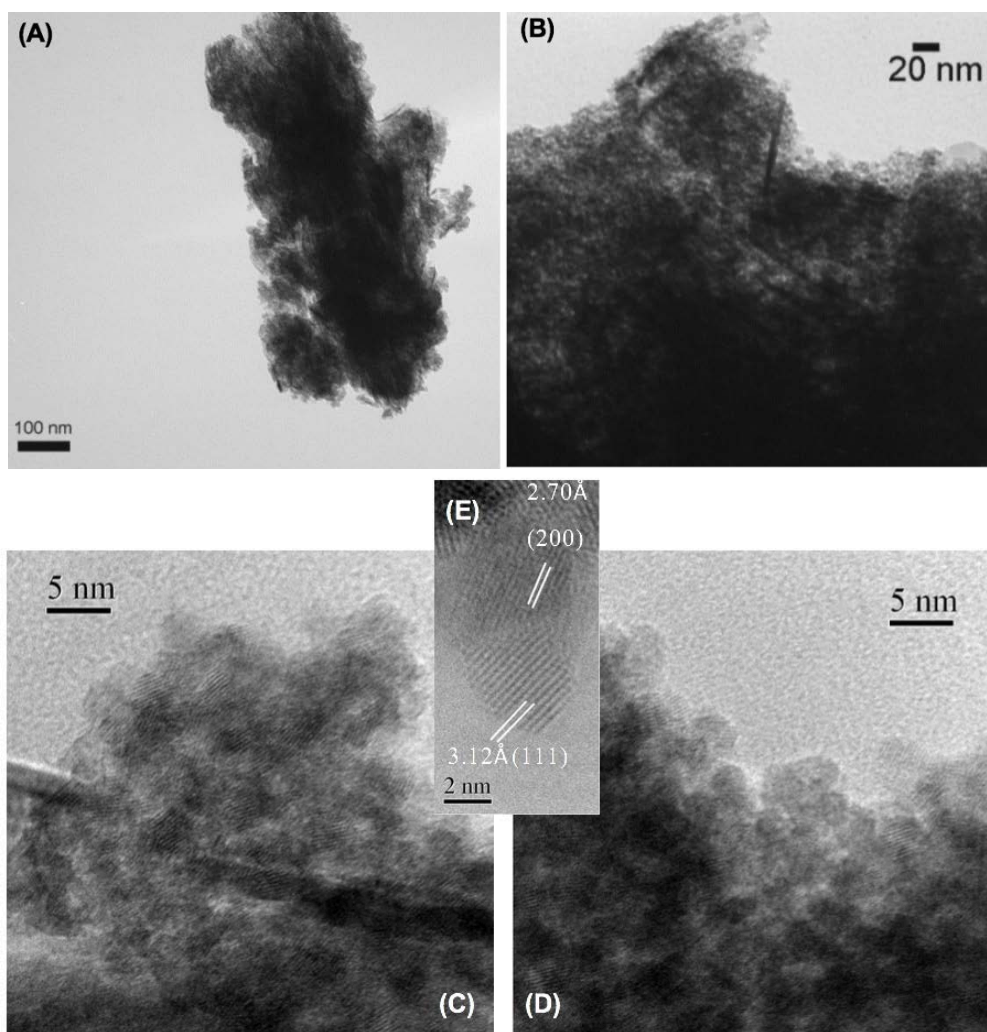


Figure S2. TEM images of the pure cerium oxide at different magnification (A,B) and at high resolution (C, D, E).

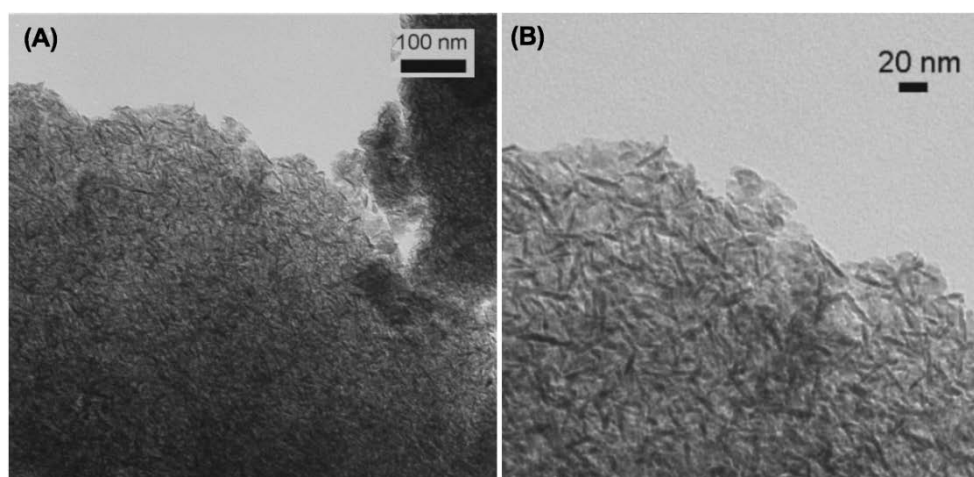


Figure S3. TEM images of the pure nickel oxide at different magnification.

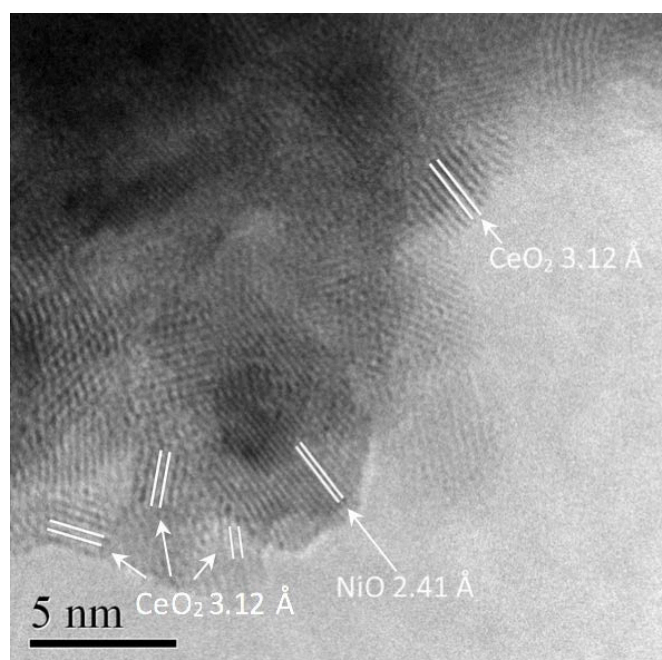


Figure S4. High Resolution TEM image of the starting 1.0NiCe sample.

X-ray photoelectron spectroscopy (XPS)

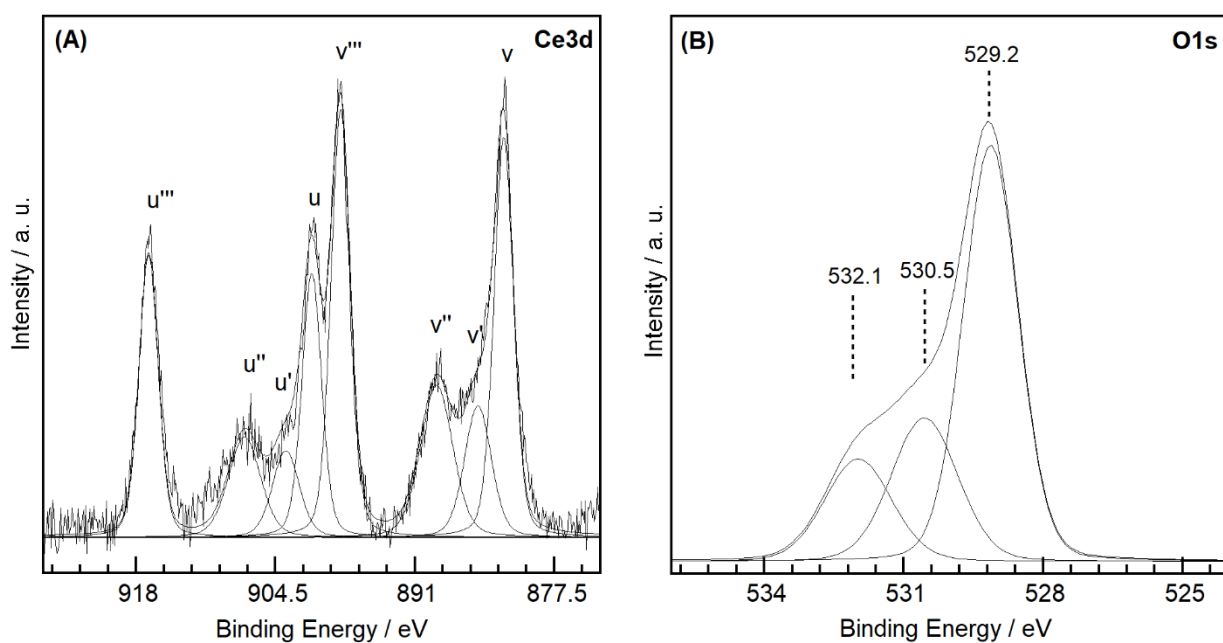


Figure S5. XPS spectra of the pure CeO₂ sample: Ce3d (A) and O1s (B) regions.

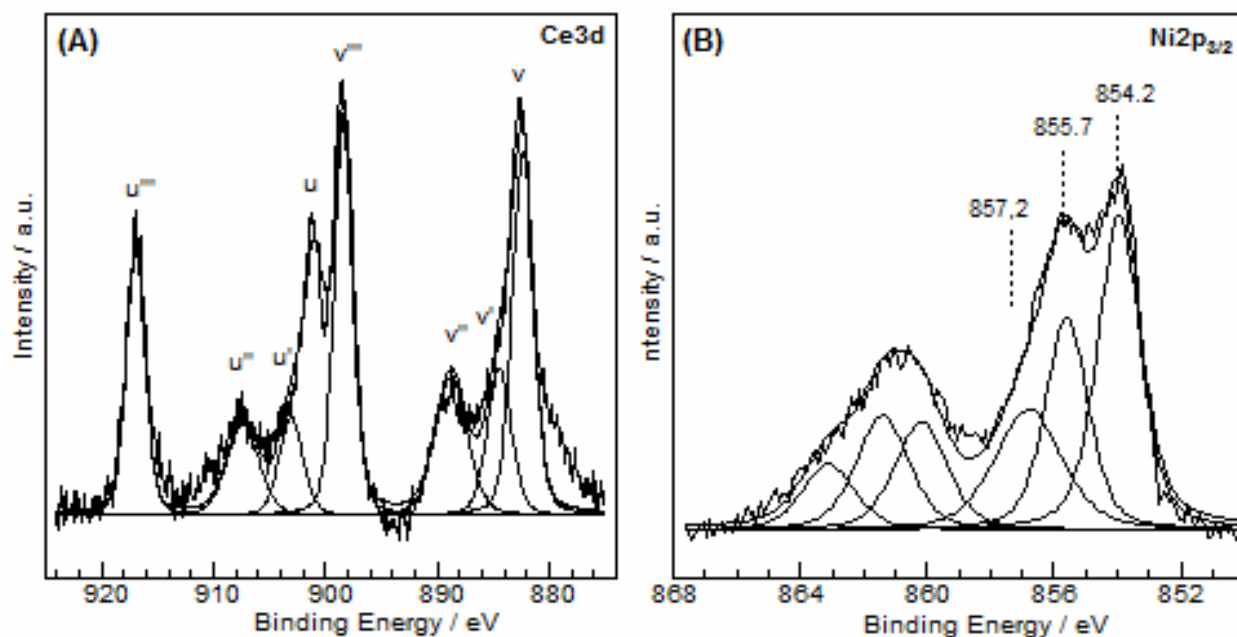


Figure S6. XPS spectra of the 1.0NiCe sample: Ce3d (A) and Ni2p_{3/2} (B) regions.

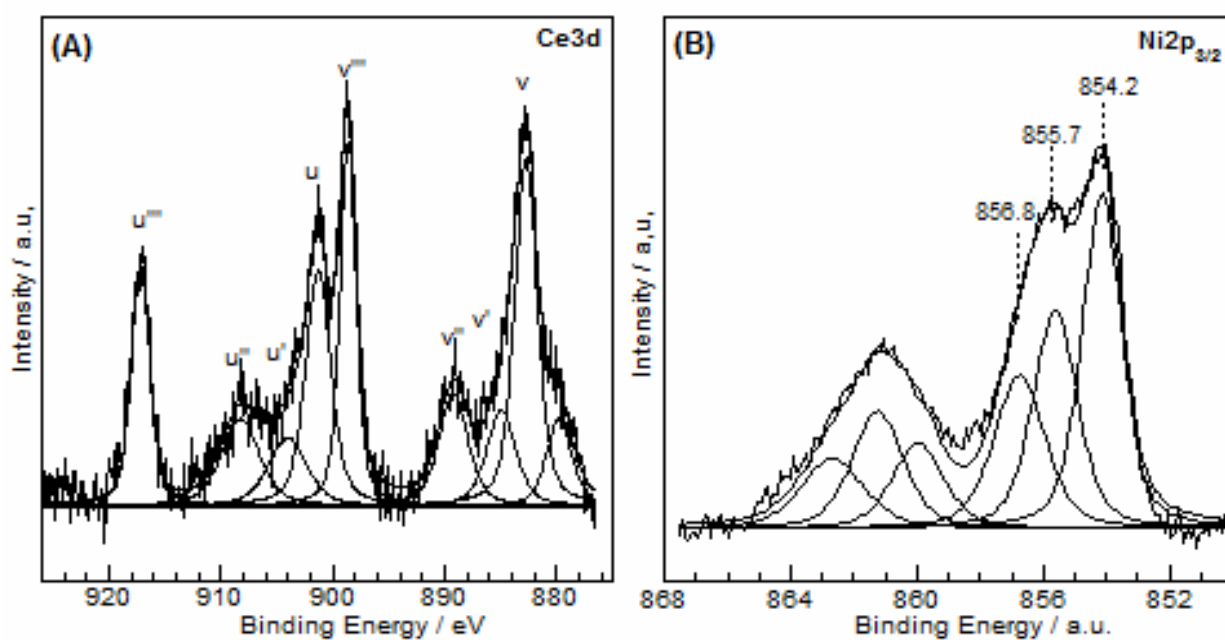


Figure S7. XPS spectra of the 2.5NiCe sample: Ce3d (A) and Ni2p_{3/2} (B) regions.

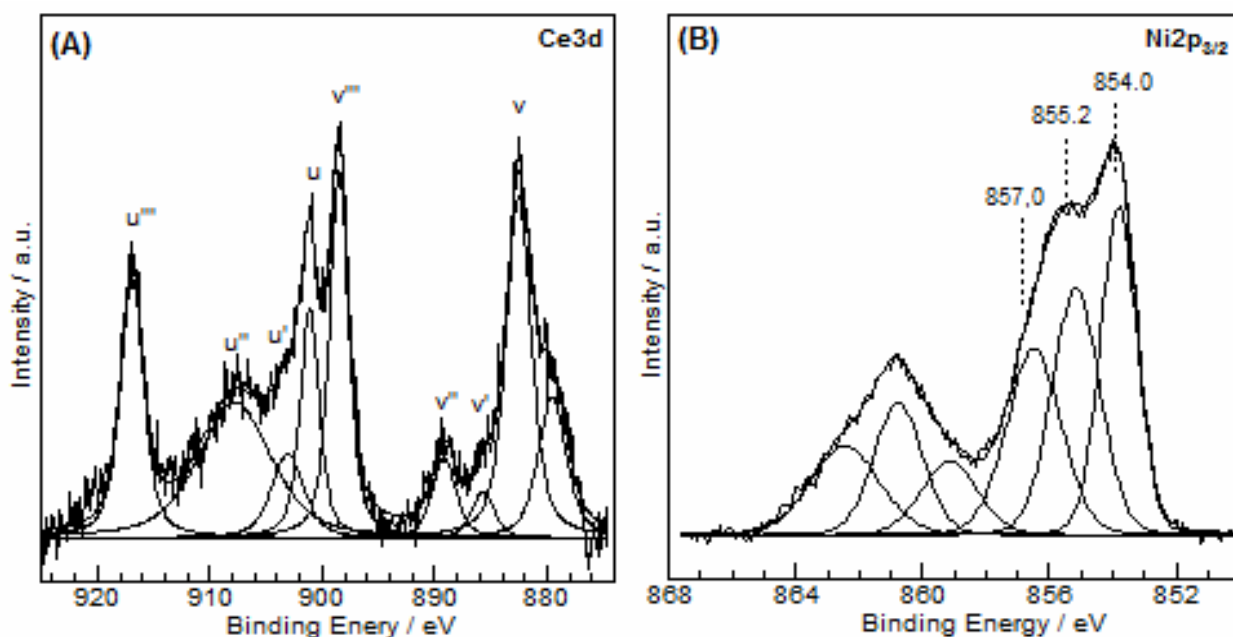


Figure S8. XPS spectra of the 4.0NiCe sample: Ce3d (A) and Ni2p_{3/2} (B) regions.

Table S1. Peak areas from curve fitting of the Ce3d region by three doublets Ce3d_{5/2}-Ce3d_{3/2} with spin-orbit splitting of 18.6 eV and Ce3d_{5/2}/Ce3d_{3/2} ratio equal to 1.515.

Sample	Ce ⁴⁺			Ce ³⁺
	v + u	v'' + u''	v''' + u'''	v' + u'
CeO ₂	32.4	17.7	31.2	10.3
0.3NiCe	27.9	16.9	26.4	15.6
1.0NiCe	42.9	25.1	39.6	20.3
2.5NiCe	19.8	8.8	16.7	9.4
4.0NiCe	16.2	9.7	15.5	8.5

Ce³⁺ fraction is determined by the ratio $\text{Ce}^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})$ where the numerator is the area of the Ce³⁺ doublets (v', u') and the denominator is the total area of the Ce3d region [Ce^{3+} (v', u') + Ce^{4+} (v, v'', v''' + u, u'', u''')]. Peak labels according to Burroughs *et al.* [48].

Table S2. Peak areas from curve fitting of the Ni3p_{3/2} main peak and related satellite (separation of 6.1 eV, 50% of the total intensity).

Sample	Ni ²⁺	Ni ³⁺
0.3NiCe	8.35	4.7
1.0NiCe	42.4	19.9
2.5NiCe	41.0	18.7
4.0NiCe	48.5	23.1

Ni³⁺ concentration is determined by the ratio $\text{Ni}^{3+}/(\text{Ni}^{2+} + \text{Ni}^{3+})$, where the numerator is the area of Ni³⁺ (NiO-CeO₂ interacting Ni species) and the denominator is the total area of the Ni3p_{3/2} region [Ni²⁺ (NiO, Ni(OH)₂) + Ni³⁺].

Thermogravimetric analysis (TGA)

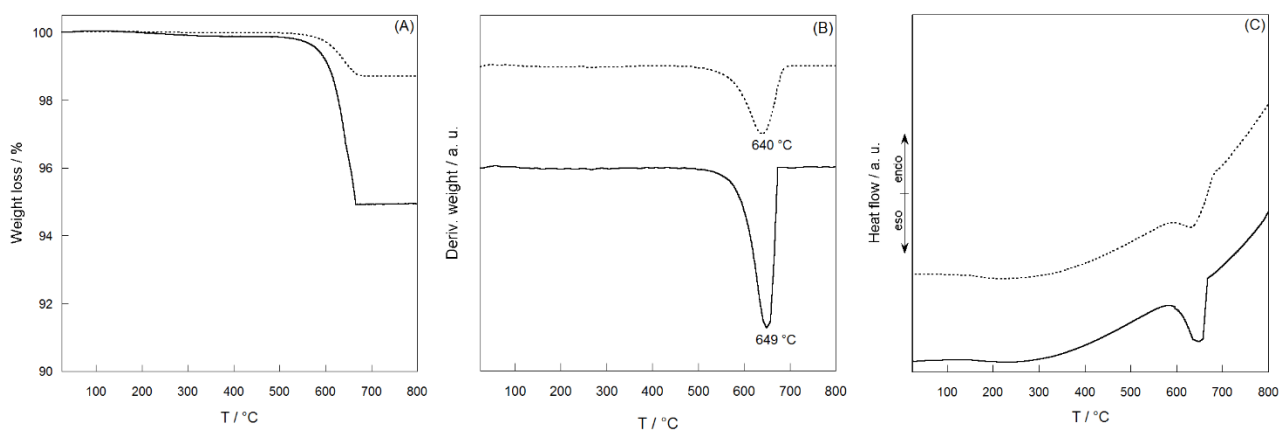


Figure S9. TGA results for the 0.3NiCe (—) and 1.0NiCe (····) catalysts after the CO and CO₂ co-methanation reaction at 300 °C, atmospheric pressure, $\text{SV} = 450000 \text{ cm}^3 \text{ h}^{-1} \text{ g}_{\text{cat}}^{-1}$, and CO/CO₂/H₂ molar ratio equal to 1/1/7. (A), TG curves; (B) DTG curves; DSC curves (C).

Temperature Programmed Desorption of CO (CO-TPD)

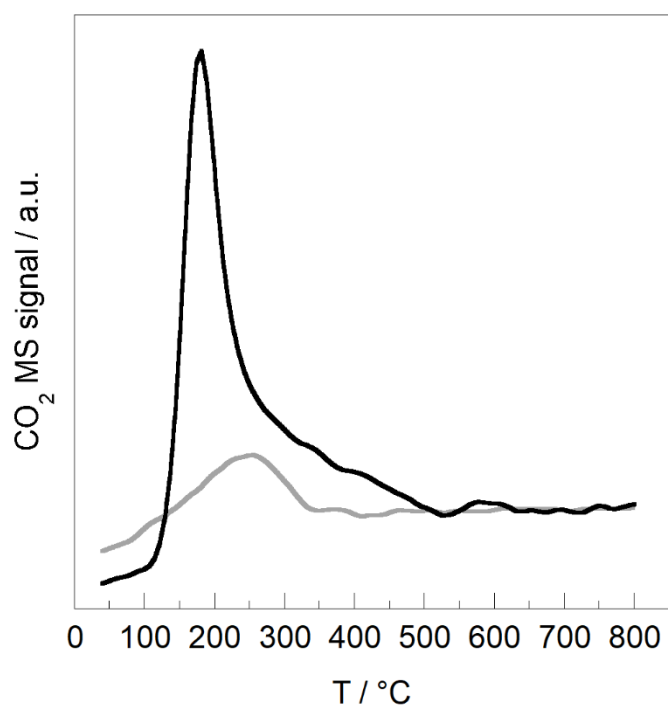


Figure S10. CO₂ ($m/z = 44$) evolution during CO-TPD experiments on 0.3NiCe (grey line) and 1.0NiCe (black line).