

Supporting Information

Elucidating the Role of Earth Alkaline Doping in Perovskite-Based Dry Reforming of Methane Catalysts

Parastoo Delir Kheyrollahi Nezhad¹, Maged F. Bekheet², Nicolas Bonmassar³, Albert Gili⁴,
Franz Kamutzki², Aleksander Gurlo², Andrew Doran⁵, Sabine Schwarz⁶, Johannes Bernardi⁶,
Sebastian Praetz,⁷ Aligholi Niaei¹, Ali Farzi¹ and Simon Penner^{3,*}

¹*Reactor & Catalyst Research Lab, Department of Chemical Engineering, Faculty of
Chemical and Petroleum Engineering, University of Tabriz, Tabriz, Iran*

²*Fachgebiet Keramische Werkstoffe/Chair of Advanced Ceramic Materials, Institut für
Werkstoffwissenschaften und -technologien, Technische Universität Berlin, Hardenbergstr.
40, 10623 Berlin, Germany*

³*Department of Physical Chemistry, University of Innsbruck, Innrain 52c, A-6020 Innsbruck,
Austria*

⁴*Institut für Chemie, Technische Universität Berlin, Sekretariat TC 8, Straße des 17. Juni
124, 10623 Berlin, Germany*

⁵*Advanced Light Source, Lawrence Berkeley National Laboratory Berkeley, California
94720, USA*

⁶*University Service Center for Transmission Electron Microscopy,
TU Wien, Wiedner Hauptstrasse 8-10, A-1040 Vienna, Austria*

⁷*Institute of Optics and Atomic Physics, Technische Universität Berlin, Hardenbergstraße 36,
10623 Berlin, Germany*

*Corresponding Author: simon.penner@uibk.ac.at, Tel: 004351250758003, Fax:
004351250758199

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Section A: Detailed XRD patterns

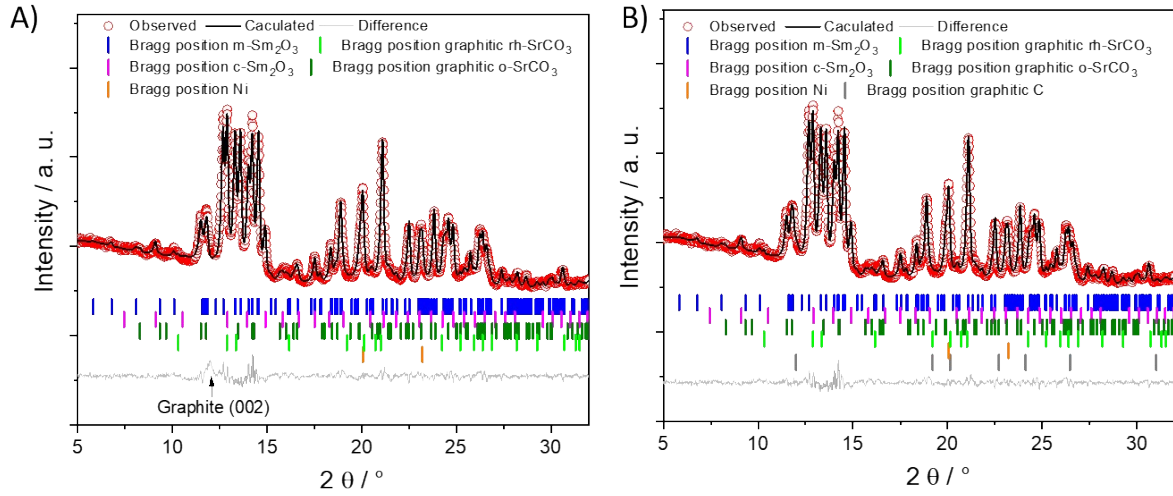


Figure S1: Structure refinement of X-ray powder diffraction data collected at room temperature for $\text{Sm}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$ Ruddlesden-Popper phase after 2 consecutive DRM cycles without (A) and with (B) the inclusion of graphitic carbon in the refinement. The observed (red circle), calculated (solid black line) and difference (solid gray line) intensities, as well as the calculated Bragg reflections (tick marks) of different crystalline phases. Wavelength: $\lambda=0.7093 \text{ \AA}$.

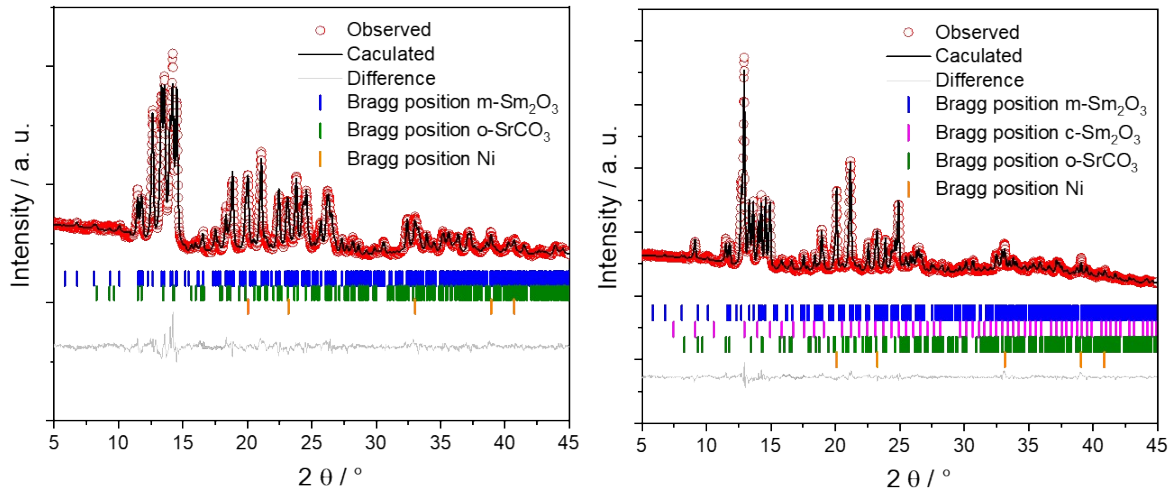


Figure S2: Structure refinement of X-ray powder diffraction data collected at room temperature for $\text{Sm}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$ Ruddlesden-Popper phase after pre-reduction in H_2 and 1 DRM cycle (A) as well as after 2 consecutive DRM cycles (B), which are followed by stability tests for 12 hours. The observed (red circle), calculated (solid black line) and difference (solid gray line)

intensities, as well as the calculated Bragg reflections (tick marks) of different crystalline phases. Wavelength: $\lambda=0.7093 \text{ \AA}$.

Section B: HRTEM images of $\text{Sm}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$ Ruddlesden-Popper phase after selected treatments in a 1:1 $\text{CO}_2:\text{CH}_4$ dry reforming methane mixture

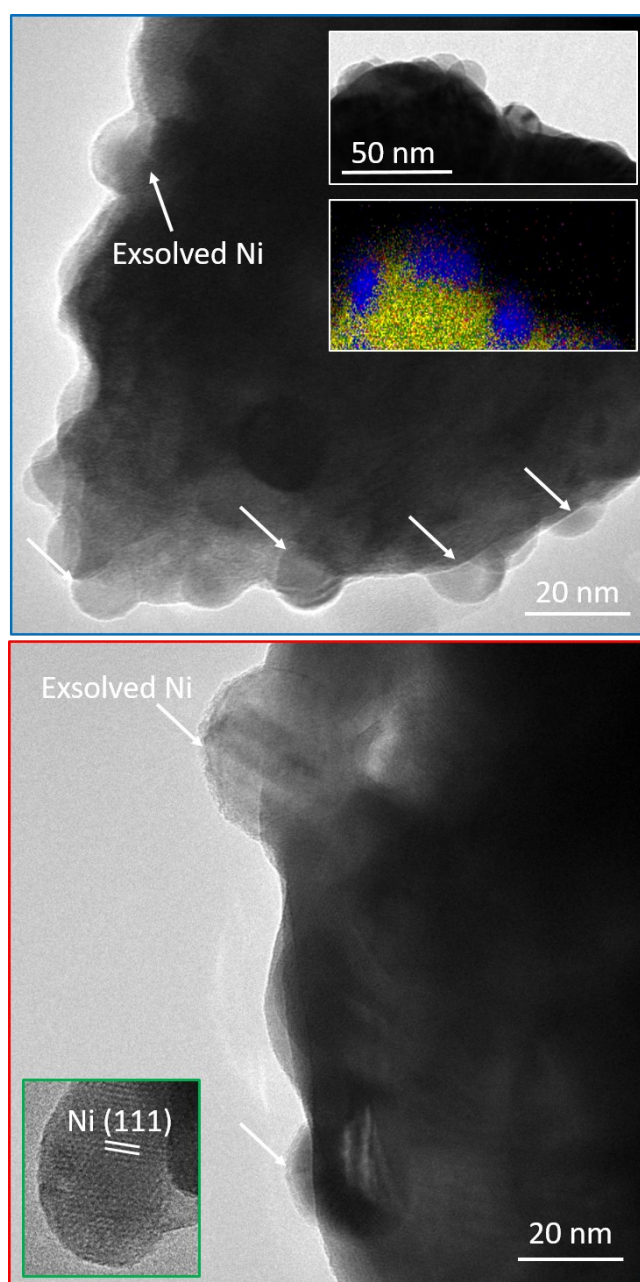


Figure S3: Detailed (HR)TEM analysis of $\text{Sm}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$ Ruddlesden-Popper phase after selected treatments in a 1:1 $\text{CO}_2:\text{CH}_4$ dry reforming methane mixture for 30 min (bottom panel, red frame) and after 1 bar flowing hydrogen for 30 min followed by a treatment in a 1:1 $\text{CO}_2:\text{CH}_4$ dry reforming methane mixture for 30 min (top panel, blue frame). Exsolved Ni as small particles decorating the rims of the much larger oxide matrix are seen in both images and have been marked by white arrows. A representative high-resolution image of a metallic Ni particle exhibiting atomically resolved $\text{Ni}(111)$ lattice fringes is shown as inset, framed in green. The inset in the right panel highlights a comparison of a BF image (top) and an overlay of EDX intensities of Sm-L (beige), Ni-K (blue), Sr-K (lilac), C-K (red) and O-K edges (green).

Section C: Coking propensity - TEM

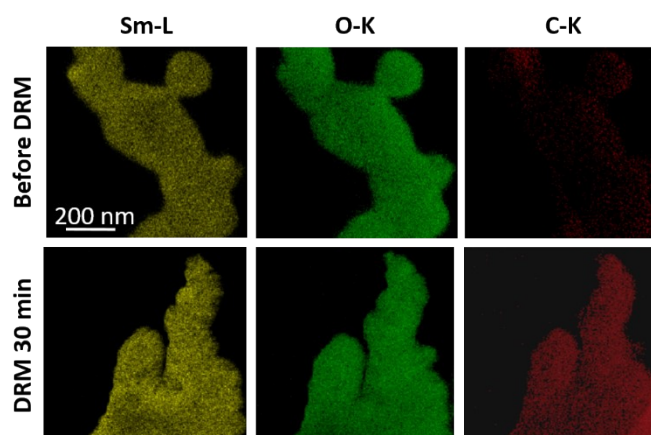


Figure S4: EDX comparison of the $\text{Sm}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$ Ruddlesden-Popper phase in the initial state (top row) and after an in situ activation treatment in an 1:1 $\text{CO}_2:\text{CH}_4$ dry reforming of methane mixture for 30 min (bottom row). The Sm-L (beige), O-K (green) and C-K edges (red) are displayed.

Section D: In situ XRD patterns during H₂-DRM

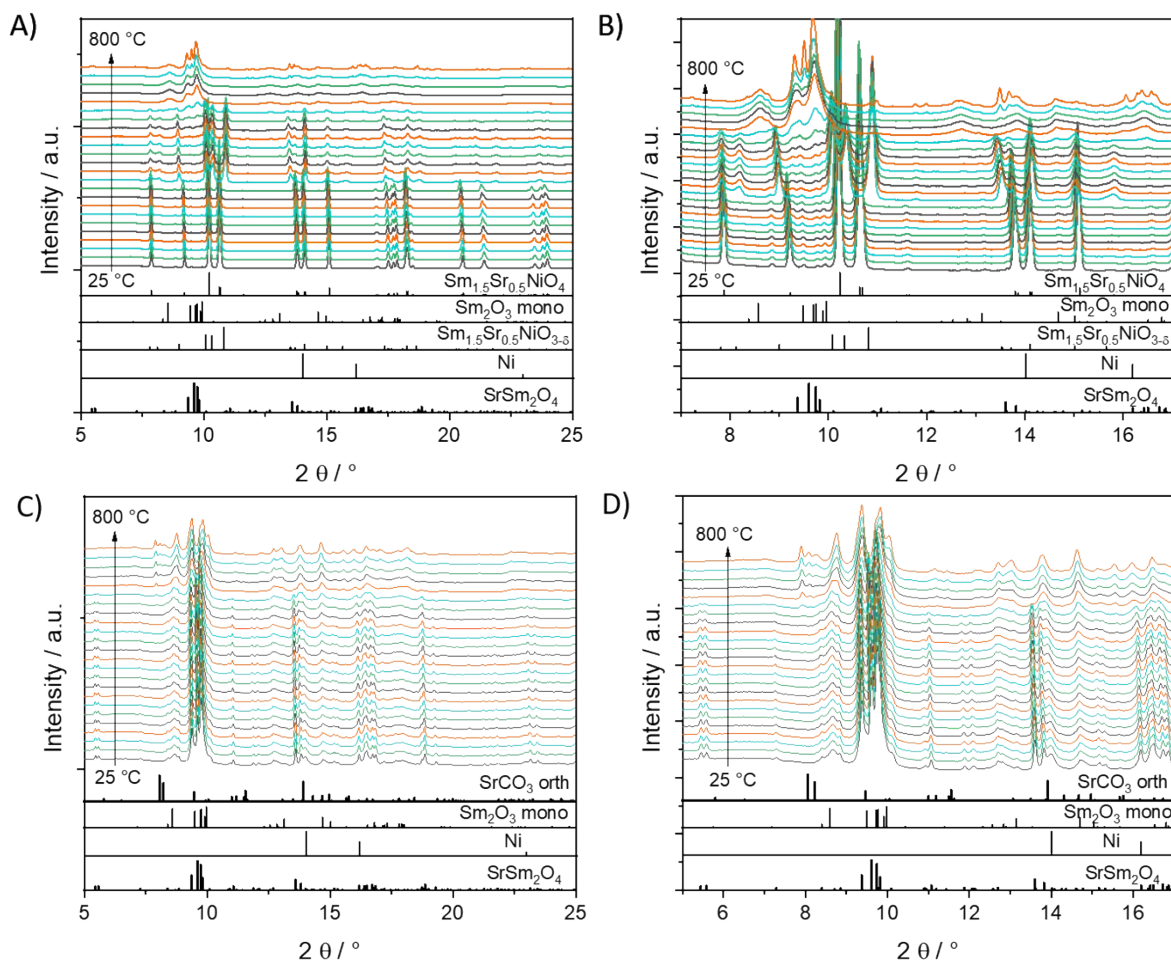


Figure S5: In situ collected XRD patterns of $\text{Sm}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$ during heating up to 800 °C in H_2 atmosphere (Panels A and B) and during re-heating in the DRM mixture (Panels C and D). Panels B and D focus on a narrower 2θ window for closer analysis. The lower panel indicates the assignment to the respective reference structures. The unindexed broad shoulder at $2\theta \sim 8.48^\circ$ corresponding to (002) reflection of graphitic carbon. Wavelength: $\lambda=0.4984 \text{ \AA}$.

Section E: In situ X-ray photoelectron spectroscopy

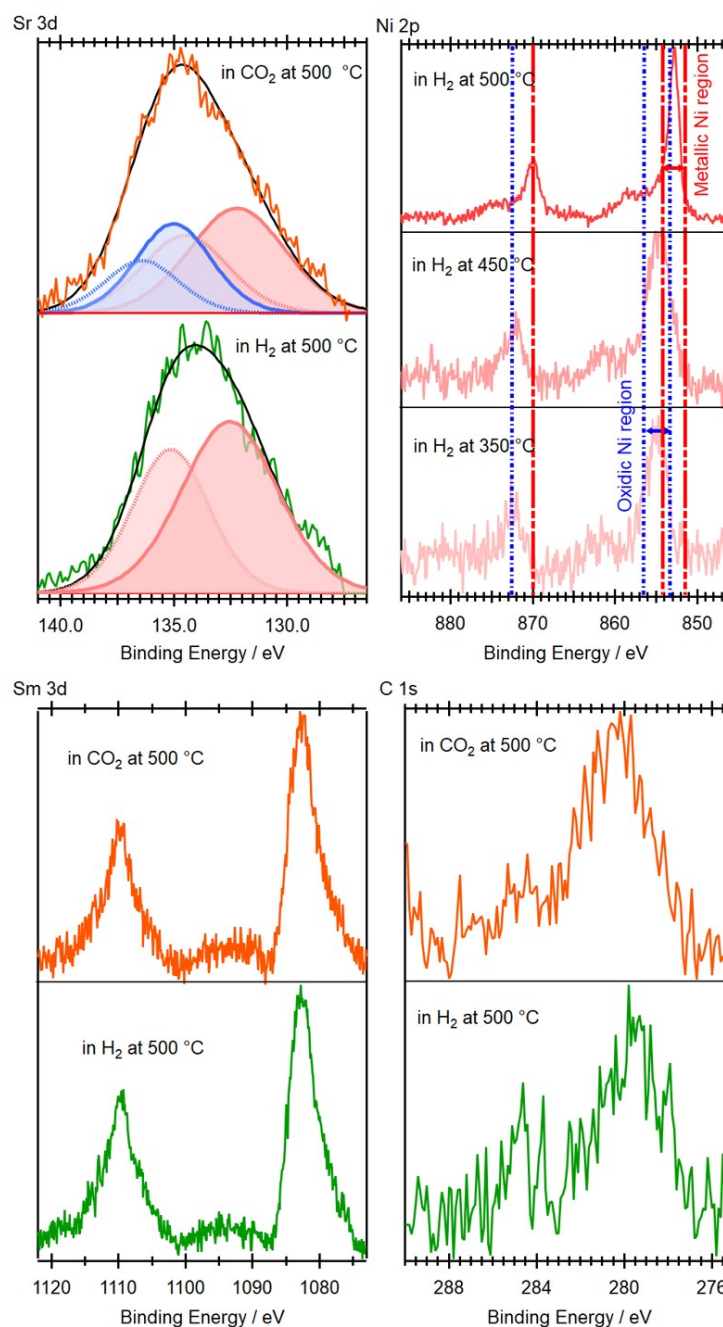


Figure S6: In situ X-ray photoelectron spectroscopy experiments on the Ni exsolution and carbonation behavior of the $\text{Sm}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$ material. Upper right panel: Evolution of the Ni 2p peak as a function of the hydrogen pre-treatment conditions. Upper left panel and bottom row: Direct comparison of the Sr 3d, Sm 3d and C 1s spectra collected at 500 °C in 0.2 mbar hydrogen and 0.2 mbar carbon dioxide. While the Sm 3d show no difference, the broader Sr 3d peak indicates the presence of a SrCO_3 phase as a consequence of reaction with carbon dioxide.

Section F: In situ XRD patterns during DRM

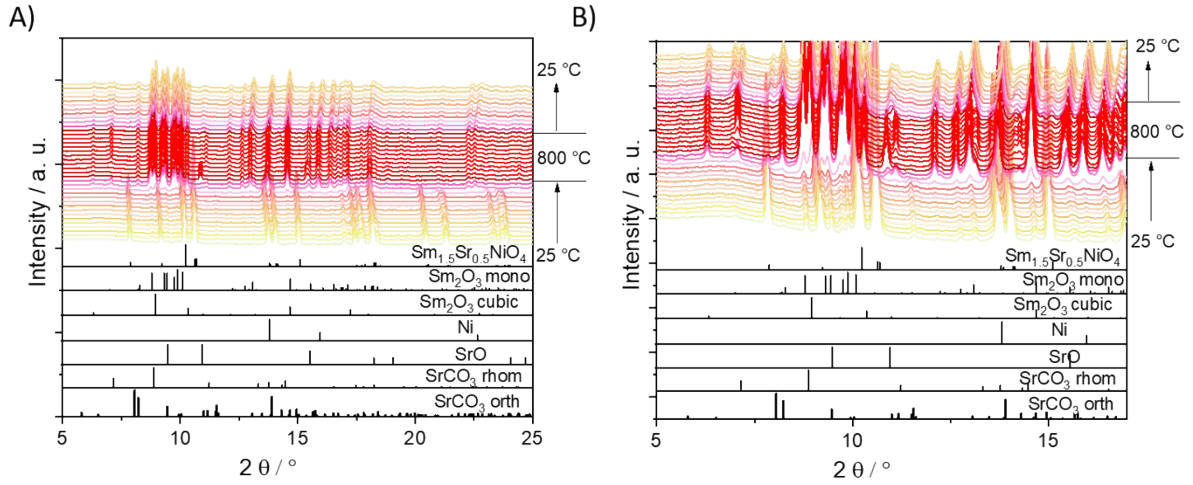


Figure S7: In situ collected XRD patterns of $\text{Sm}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$ during heating up to 800 °C in DRM atmosphere for 10 min before cooling to room temperature. Panels B focus on a narrower 2 θ window for closer analysis. The lower panel indicates the assignment to the respective reference structures. Wavelength: $\lambda=0.4984$ Å.

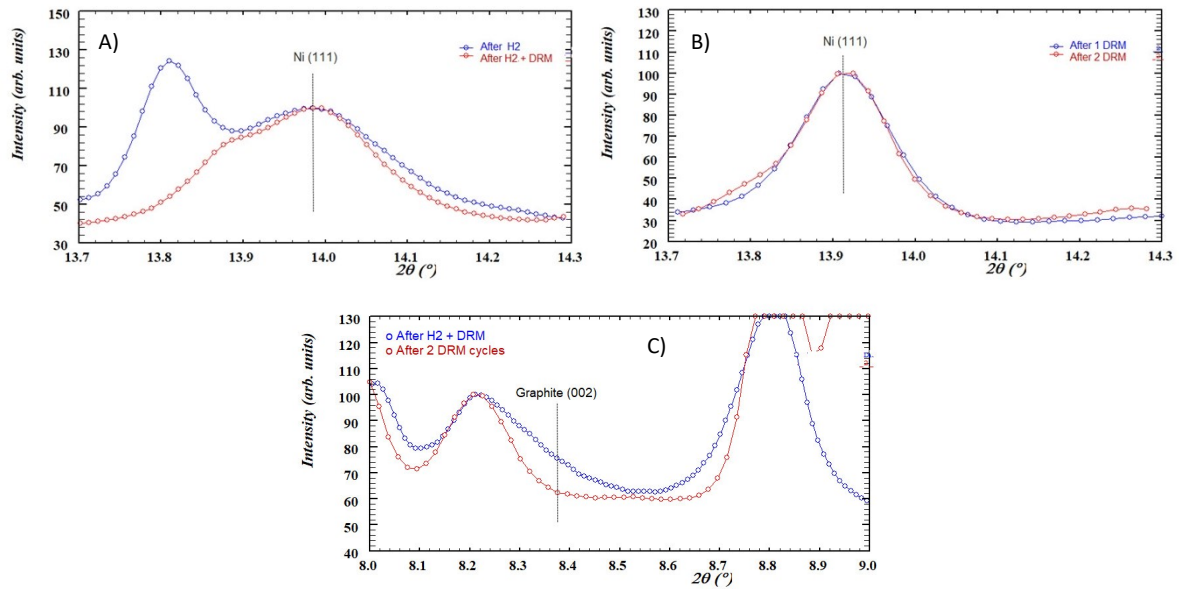


Figure S8: Comparison between the Ni (111) reflections in the collected XRD patterns of $\text{Sm}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$ after cooling to room temperature from pre-reduction in H_2 and 1 DRM cycle (A), and from two consecutive cycles of DRM (B). Panel C shows the difference between the

collected XRD pattern of the recovered sample after two experiments. Wavelength: $\lambda=0.7093$ Å.

Section G: TEM characterization after one DRM cycle

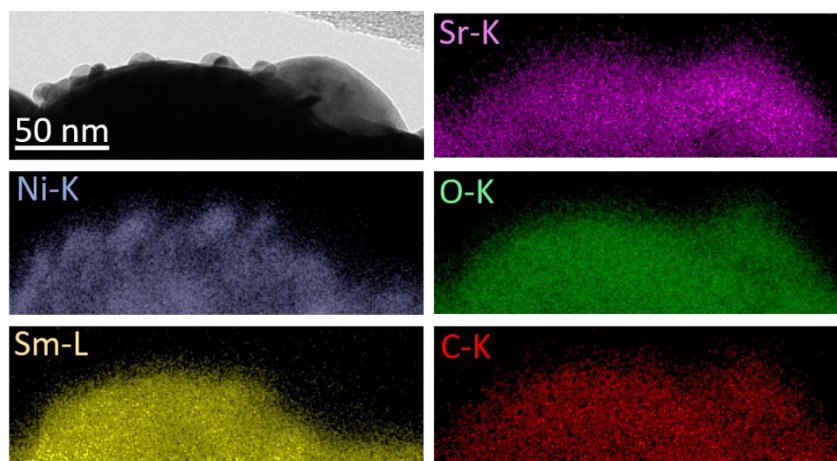


Figure S9: TEM/EDX analysis of the $\text{Sm}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$ Ruddlesden-Popper phase after an in situ activation treatment in an 1:1 $\text{CO}_2\text{:CH}_4$ dry reforming methane mixture for 30 min (bottom row). Top left: Bright-field overview image. The Sm-L (yellow), O-K (green) and C-K edges (red), Sr-K (magenta) and Ni-K (blue) edge intensities are displayed.

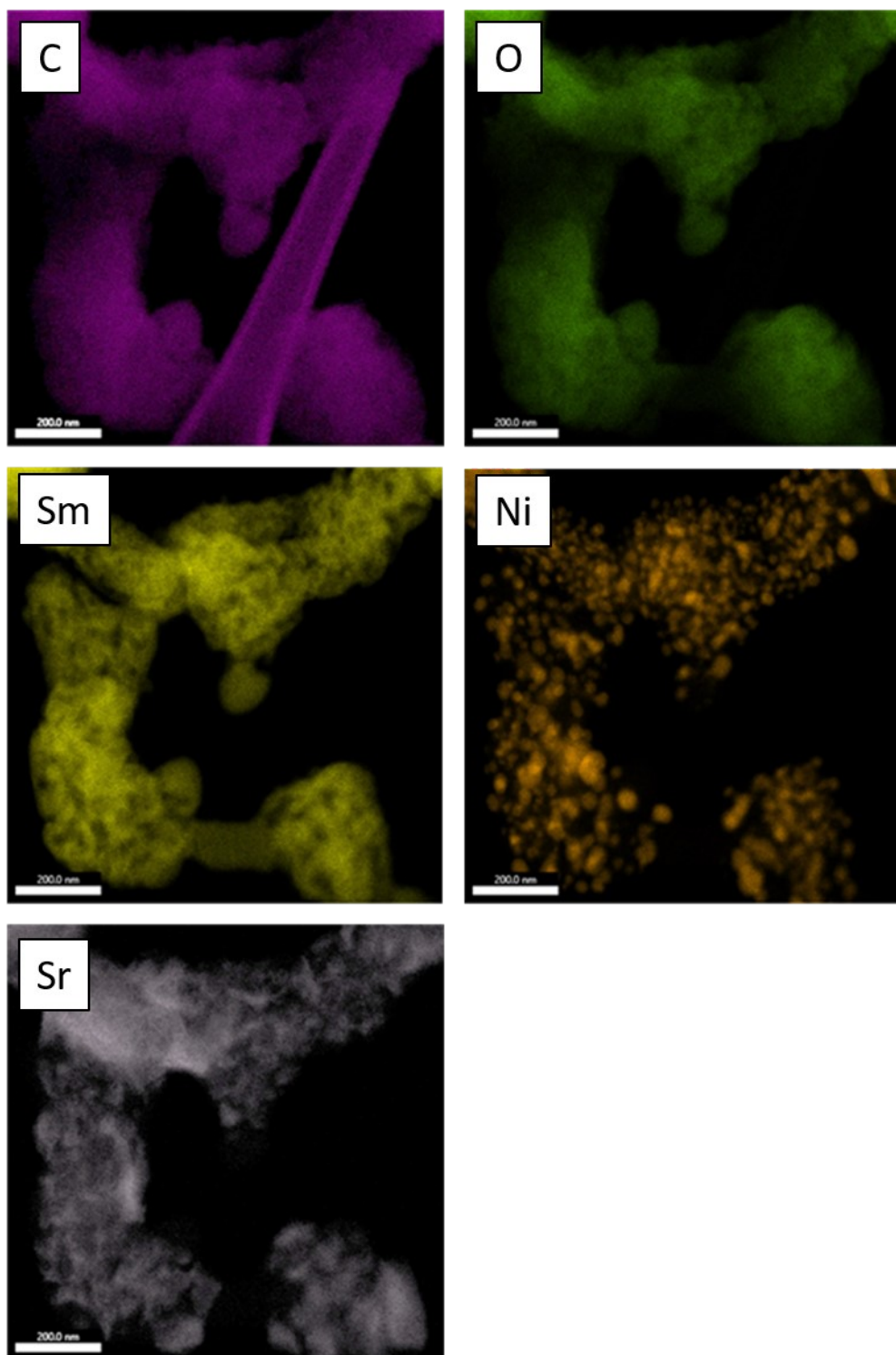


Figure S10: EDX analysis of $\text{Sm}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$ after a DRM reaction at 800 °C followed by an isothermal period for 30 min at 800 °C. Sm-L (yellow), Sr-K (purple), O-K (green), C-K (pink) and Ni-K (orange) intensities are shown. Overlay shown in Figure 7.

Section H: X-ray photoelectron spectra collected after selected pre-treatments

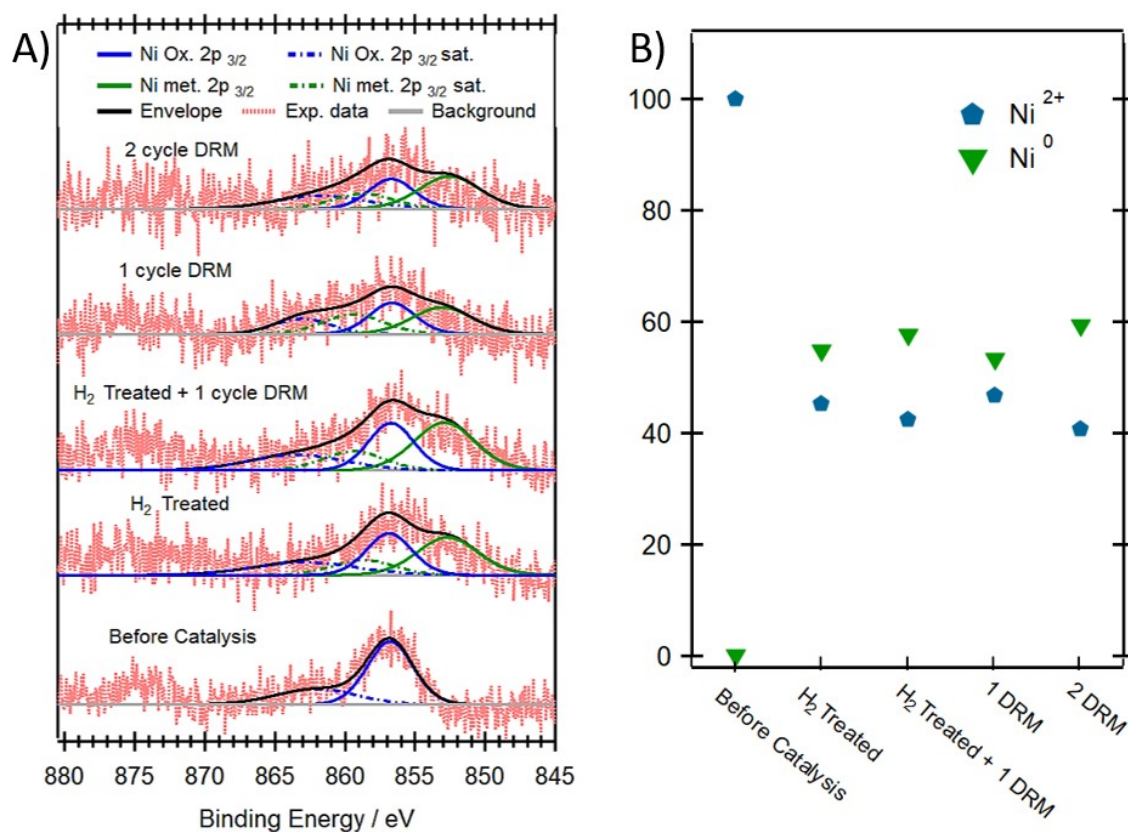


Figure S11: Panel A: High-resolution X-ray photoelectron spectra of the Ni 2p region in the initial state and after selected pre-reduction and self-activation treatments. The Ni 2p region has been deconvoluted into individual Ni components. Panel B: Quantitative analysis (in at %) of Ni^{2+} and Ni^0 as a function of treatment.

Table S1: Quantitative analysis (in at%) of Ni^{2+} and Ni^0 as a function of treatment.

XPS fitting data (Atom %) Ni 2p region for catalysts	Ni 2p _{3/2} (Ni^{2+})	Ni 2p _{3/2} (Ni^0)
Before catalysis	100	0
H ₂ Treated (800 °C)	45.20	54.8
H ₂ Treated (800 °C) + 1 DRM (800 °C)	52.5	57.5
1 st cycle DRM (800 °C)	46.7	53.3
2 nd cycle DRM (800 °C)	40.7	59.3

Section I: X-ray absorption spectra of the normalized Sm LIII and Sr-K edges after selected treatments

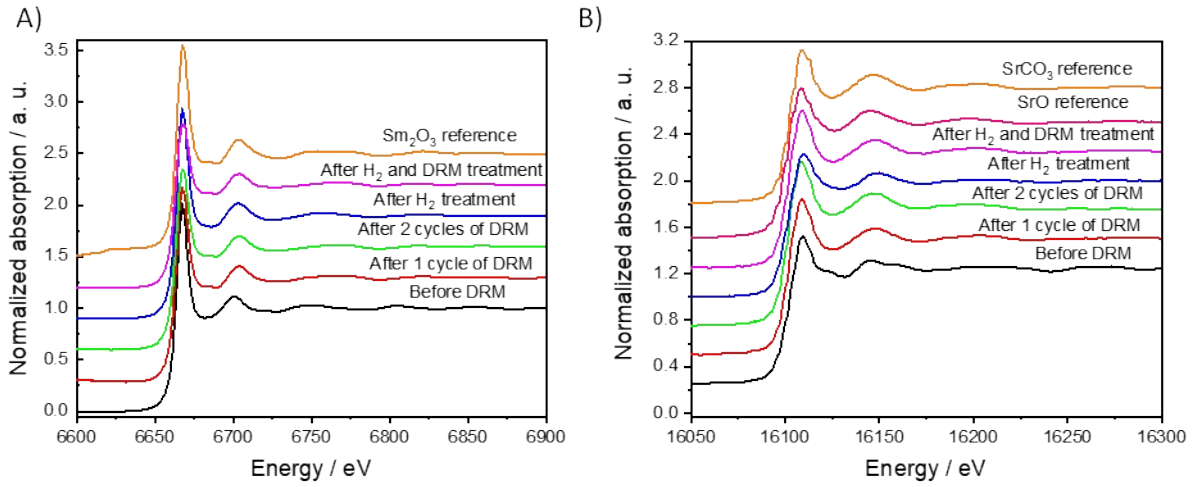


Figure S12: Panel A: Normalized Sm LIII-edge X-ray absorption near-edge structure (XANES) of $\text{Sm}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$ material before and after different DRM experiments. The spectra are compared with that of Sm_2O_3 as a reference material. Panel B: Normalized Sr K-edge X-ray absorption near-edge structure (XANES) of $\text{Sm}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$ material before and after different DRM experiments. The spectra are compared to that of SrO and SrCO_3 as a reference material.

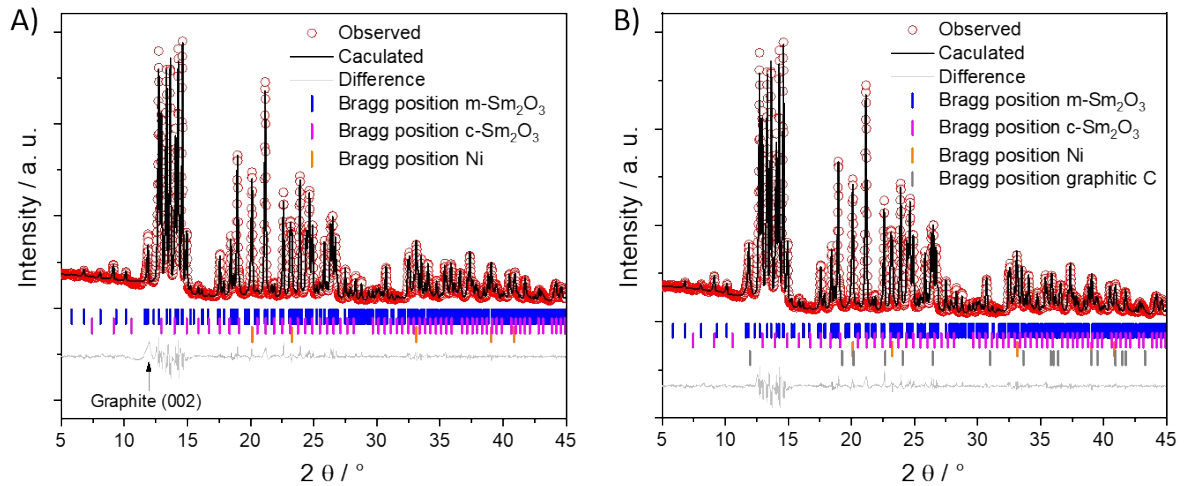


Figure S13: Structure refinement of X-ray powder diffraction data collected at room temperature for $\text{Ni}/\text{Sm}_2\text{O}_3$ after hydrogen pre-reduction followed by one DRM cycle without (A) and with (B) the inclusion of graphitic carbon in the refinement. The observed (red circle),

calculated (solid black line) and difference (solid gray line) intensities, as well as the calculated Bragg reflections (tick marks) of different crystalline phases. Wavelength: $\lambda=0.7093$ Å.

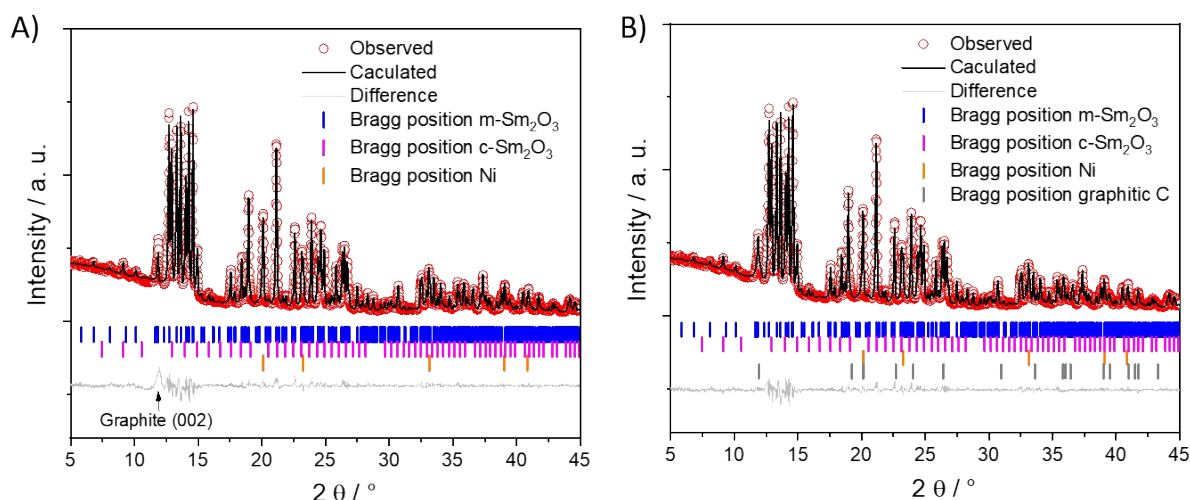


Figure S14: Structure refinement of X-ray powder diffraction data collected at room temperature for Ni/Sm₂O₃ phase after 2 consecutive DRM cycles without (A) and with (B) the inclusion of graphitic carbon in the refinement. The observed (red circle), calculated (solid black line) and difference (solid gray line) intensities, as well as the calculated Bragg reflections (tick marks) of different crystalline phases. Wavelength: $\lambda=0.7093$ Å.

Section J: Assessment of Diffusion Limitation

We evaluated the Weisz-Prater criterion for catalysts to prove the absence of diffusion limitation in this work. This criterion is a factor in determining the importance of diffusional limitation:

- $$\Phi = \frac{r_{obs}L^2}{D_{eff}C_0}$$
1. For $\Phi < 1$ there is no pore diffusion limitation
 2. For $\Phi \geq 1$ there is strong pore diffusion limitation,

where r_{obs} is the observed reaction rate in the experiments, L is the characteristic length which is $d/6$ for spherical particles, D_{eff} is the effective diffusion coefficient, C_0 is the concentration on the catalyst surface. According to the previous descriptions and disregarding the external diffusion resistance (because the catalyst is dispersed with a high void fraction along the catalytic bed and diluted with quartz wool which gives the ability for gas to penetrate easily (concentration on the surface equal to the gas phase), we continue with the calculation.

To calculate D_{eff} [5]:

$$D_{eff} = \frac{D_{12}\theta}{\tau},$$

where τ is tortuosity factor which is around 2-3 based on the different references [5], θ is the void fraction in the catalyst and D_{12} is the diffusion coefficient of the gases penetrating in porous media along each other.

$$D_{12} = \frac{0.001858T^{3/2} \left[\frac{M_1 + M_2}{M_1 M_2} \right]^{1/2}}{P\sigma_{12}^2\Omega_D},$$

D_{12} is calculated using the following equation:

where T is the temperature in Kelvin, M is molecular weight of gases, P is pressure which is 1 atm in our study, Ω is the collision integral, a function of kT/ε_{12} , ε and σ are the force constants in the Leonard-Jones potential function, k is the Boltzmann constant $= 1.38 \times 10^{-23} \text{ kgm}^2\text{k}^{-1}\text{s}^{-2}$,

$$\varepsilon_{12} = \sqrt{\varepsilon_1 \varepsilon_2} \quad \text{and} \quad \sigma = \frac{1}{2}(\sigma_1 + \sigma_2).$$

Using the handbooks and references [5] ε and σ for Ar as carrier gas and CH_4 and CO_2 as reactants present in the gas mixture has been gathered and calculations to evaluate D_{eff} and then the Weisz-Prater criterion has been calculated. The results are gathered in the following tables:

Lennard-Jones Force constants					
gas	ε/k $k=1.38 \times 10^{-23} \text{ kgm}^2\text{k}^{-1}\text{s}^{-2}$	ε	$\varepsilon_{12}=\sqrt{\varepsilon_1 * \varepsilon_2}$	$\sigma(\text{\AA})$	$\sigma = \frac{1}{2}(\sigma_1 + \sigma_2)$
Ar	93.3	1.28754×10^{-21}		3.542	
CH ₄	148.6	2.0507×10^{-21}	CH ₄ in Ar	3.758	CH ₄ and Ar
			1.6249×10^{-21}		3.65
CO ₂	195.2	2.6937×10^{-21}	CO ₂ in Ar	3.941	CO ₂ and Ar
			1.8623×10^{-21}		3.7415

For CH₄ and CO₂ diffusion in Argon through the catalyst, we have calculated the following values based on the above relations and tables in hand books [5], for 3 temperature of studied temperature range are as follows:

T(k)	$kT/\varepsilon_{12} \text{ CH}_4 \text{ in Ar}$	$kT/\varepsilon_{12} \text{ CO}_2 \text{ in Ar}$	$\Omega \text{ CH}_4 \text{ in Ar}$	$\Omega \text{ CO}_2 \text{ in Ar}$
873	7.41424	6.469097	0.78205	0.80191
973	8.26352	7.210117	0.76708	0.78573

1073	9.1128	7.951136	0.754111	0.77212
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According to the mentioned relations and calculated values, further calculations are as follows:

For example, for 1073 K (where the diffusion limitation would be crucial, as at higher temperatures the reaction is faster):

- CH₄ diffusion in Ar inside the catalyst:

$$D_{12} = ((0.001858 * (1073^{1.5}) * ((16 + 39.948) / (16 * 39.948))^{0.5})) / ((3.758^2) * 0.754111)$$

$$D_{12} = 1.8142 \text{ cm}^2/\text{s}$$

- CO₂ diffusion in Ar inside the catalyst:

$$D_{12} = ((0.001858 * (1073^{1.5}) * ((44 + 39.948) / (44 * 39.948))^{0.5})) / ((3.941^2) * 0.77212)$$

$$D_{12} = 1.1901 \text{ cm}^2/\text{s}$$

With having τ the tortuosity factor which is around 2-3 based on the different references [5] and θ the void fraction of catalyst which is equal to 0.4 we can calculate D_{eff} :

CH₄ diffusion in Ar inside the catalyst:

$$D_{\text{eff}} = 0.36284 \text{ cm}^2/\text{s}$$

CO₂ diffusion in Ar inside the catalyst:

$$D_{\text{eff}} = 0.238 \text{ cm}^2/\text{s}$$

$$D_{\text{eff ave}} = 0.3004 \text{ cm}^2/\text{s}$$

Afterwards one can calculate the $\Phi = \frac{r_{\text{obs}} L^2}{D_{\text{eff}} C_0}$

According to the results the particle size assuming them as spherical pellets, is below the range of 0.1 mm and at each temperature we have the observed rate which is the change in gas concentration over the time the gas is passing over the catalyst. The C_0 is the concentration on the surface of the catalyst, considering no external diffusion limitation the concentration in the gas phase is the same as the concentration on the catalyst surface.

r_{obs} is also can be calculated according to the proved equations in chemical reactors: $r_{obs}=C_0X_A/t$ in which X is conversion and t is the residence time.

$t=V/v$, $v=100$ ml/min or 1.66×10^{-6} m³/s in our study through a reaction bed with volume of about 10^{-6} m³. So, $t=0.6$ s.

For example, at 1073 k, $X_{at\ 1073\ k}$ for catalysts is around 0.9.

After simplifying we result:

$$\Phi = \frac{r_{obs}L^2}{D_{eff}C_0} = \frac{\frac{C_0X_A}{t}L^2}{D_{eff}C_0} = \frac{X_A}{t} \frac{L^2}{D_{eff}}$$

$d_{particle}$ is around 0.01 cm which is clear from the image and has been proved by sieving the powder through different meshes. $L=d_{particle}/6$ is the characteristic length for diffusion inside pores.

$$\Phi = \frac{X_A \times \left(\frac{0.01\ cm}{6}\right)^2}{\frac{0.6\ s}{0.3004\ \frac{cm^2}{s}}}$$



After all calculations at 1073 K: $\Phi=0.0000138704$.

All of the calculated values are well below 1. As all values are $\Phi < 1$, there is no diffusion limitation in our catalytic tests. This conclusion proves that for catalysts loaded to the reactor in their powder form and exhibiting small particle sizes, diffusion resistance is not important. The calculations for any other temperatures is in the same value region and still result in $\Phi < 1$.

References

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