Perovskites as Precursors for Ni/La₂O₃ Catalysts in the Dry Reforming of Methane: Synthesis by Constant pH Co-Precipitation, Reduction Mechanism and Effect of Ru-Doping

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Abstract. LaNiO₃ perovskite is an interesting precursor for Ni/La₂O₃ catalysts for the dry reforming of methane at high temperatures. Precursors have been synthesized by co-precipitation without, with 2.5 at%, and with 5 at% Ru doping. The presence of Ru leads to a stabilization of the perovskite structure and hinders the decomposition into NiO and Ruddlesden-Popper mixed oxides La_{*n*+1}Ni_{*n*}O_{3*n*+1}, which was observed for the Ru-free sample upon calcination at 1000 °C (*n* = 3). Upon reduction in hydrogen, a mechanism involving at least two steps was observed and the first major step was identified as the partial

reduction of the precursor leading to a LaNiO_{2.5}-like intermediate. The second major step is the reduction to Ni metal supported on La₂O₃ independent of the Ru content of the catalyst. In the presence of Ru, indications for Ni-Ru alloy formation and for a higher dispersion of the metallic phase were found. The catalytic activity in DRM of the catalyst containing 2.5 % Ru was superior to the catalysts with more or without Ru. Furthermore, the propensity of coke formation was reduced by the presence of Ru.

Introduction

There is a tremendous interest in catalytic carbon dioxide conversion reactions, such as the dry reforming of methane [DRM, Equation (1)], which produces syngas from methane and carbon dioxide and is a highly endothermic reaction usually conducted at high temperatures.

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2; \Delta_R H^0 = 247 \text{ kJ} \cdot \text{mol}^{-1}$$
(1)

Thus, a catalyst for dry reforming requires in addition to high activity also high thermal stability, mechanical resistance, and, in particular, high resistance against coking.^[1] In addition to noble metal-based catalysts (Rh, Ru, Pd, Pt, Ir), also Nibased catalysts were found to be catalytically active, but they are much more sensitive to coke depositions than their noble metal counterparts.^[2] It is thus interesting to combine the two aspects of high activity and coking stability in doped Ni-based catalysts modified by small amounts of noble metal. A similar effect is discussed, e.g., for Au decoration of Ni catalyst, which leads to a reduction coking in the steam reforming of methane

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/zaac.201700141 or from the author. due to the decoration of Ni surface steps hindering graphite nucleation.^[3] A positive effect of addition of small amounts of noble metal has also been observed for the dry reforming of coke oven gas over Ni catalysts.^[4] *Mo* et al.^[5] recently reported a precursor synthesis method yielding a Ni-La₂O₃/SiO₂ catalyst that did not show any coking over 100 h of operation.

An attractive class of catalyst precursors are perovskite-type oxides with the general formula ABO_3 as they provide a kind of bifunctionality.^[6] The larger cation A is usually unreducible and - in form of its oxide - responsible for the thermal resistance of the material while the cation B, typically Nickel, can be reduced to its metallic form and is associated with the catalytic activity. For DRM, LaNiO₃ perovskites were already investigated and turned out to be interesting precursors for active and stable catalysts.^[7] However, the precursor chemistry is not always straightforward and among the challenges of this system is the undesired phase segregation into NiO and mixed oxides of a Ruddlesden-Popper (RP) series with the general formula La_{n+1}Ni_nO_{3n+1}.^[8] Some reports on thermodynamic data for the La-Ni-O system are available, and in general the exact phase behavior is dependent on the oxygen partial pressure.^[9]

For the synthesis of such mixed oxides different approaches are used,^[10] e.g. the Pechini method,^[7d,11] thermal decomposition of amorphous citrate precursor,^[7a] self-combustion (autoignition),^[7b,7c] hydrothermal flow co-precipitation,^[12] as well as decreasing pH co-precipitation.^[7e] The important role of the synthesis method for LaNiO₃-derived DRM catalysts has been recently reported by *Pereniguez* et al.^[13] and *Singh* et al.^[14]

In this study, we investigated the LaNiO₃ perovskite precursor system and used Ru-doping for an improved coking suppression in DRM. La-Ni-(Ru) perovskites were obtained from an amorphous co-precipitate synthesized at constant pH, which in the following synthesis step was subjected to high-tempera-

ture calcination to crystallize the mixed oxide. Constant pH co-precipitation is a method that often turned out to be superior to decreasing or increasing pH co-precipitation due to better mixing, higher reproducibility and better scalability of the synthesis. It has been recently used by our group to synthesize another class of Ni-based DRM catalysts – Ni/MgAl₂O₄.^[15] To the best of our knowledge no constant pH co-precipitation was used before for the La-Ni perovskite catalyst precursor system.

Herein, we report the synthesis and solid state chemistry of the precursor, with a particular focus on the reduction mechanism of such perovskites to understand the formation of Ni as active component for DRM at high temperatures. In general, two distinct reduction peaks are observed using temperatureprogrammed reduction (TPR) of La-Ni perovskites.[13-14] In the literature, there are two different interpretations of this behavior. Gallego et al.^[7c] reported a 3-step reduction of LaNiO₃ based on XRD. On the other hand, Guo et al.^[7d] and Ruckenstein et al.^[16] reported two main reduction processes. These authors observed that after reduction at 450-500 °C the perovskite is still present. Thus, they suggested that the first peak belongs to the reduction of initially amorphous NiO, followed by the reduction of LaNiO₃ itself. This uncertainty of the intermediate phase during reduction and the potential of Ru doping motivated the presented study.

Results and Discussion

Co-Precipitation

Mixed Ni-La-Ru oxides were synthesized from co-precipitated precursors using the constant pH approach. A mixed metal nitrate solution was continuously fed into a glass reactor, while Na₂CO₃ solution was simultaneously dosed as precipitating agent to keep the pH constant at a value of 8. The synthesis protocol is presented and briefly discussed in the Supporting Information (Figure S1). The [La]:[Ni+Ru] ratio was 1:1 and the Ru content was varied from 0 over 2.5 to 5.0° at% of the total metal content to investigate its role in the phase evolution of the oxide precursor and in the final catalyst.

All obtained samples were X-ray amorphous directly after co-precipitation, washing, and drying (Figure S2, Supporting Information). The composition of the dried precursors, as determined by XRF (Table 1), is in good agreement with the nominal values. The samples are labeled in the following according to the Ru content as Ru-0, Ru-2.5 and Ru-5. Calcined samples are denoted as Ru-N-T with N corresponding to the Ru content and T to the calcination temperature in °C.

Table 1. Metal contents in at % determined by XRF of dried precursors; Nominal values: La: 50 at %, Ni: (50 - x) at %, x = Ru content.

	Ru-0 (0 at % Ru)	Ru-2.5 (2.5 at % Ru)	Ru-5 (5 at % Ru)
La	50.00 ± 0.15	49.85 ± 0.07	49.58 ± 0.15
Ni	50.00 ± 0.1	47.81 ± 0.05	45.13 ± 0.1
Ru	-	2.34 ± 0.01	5.29 ± 0.05

Investigation of Calcination and Calcined Materials

The co-precipitated precursors had to be calcined to be transferred into the desired perovskites. Beforehand, the decomposition behavior of the precursors was investigated by thermogravimetry coupled with online mass-spectrometry (TG-MS). Figure 1 shows exemplarily the TG-MS curves for Ru-2.5 (data for Ru-0 and Ru-5 can be found in Figure S3, Supporting Information). The weight decreased continuously up to 670 °C accompanied by several processes of H₂O and CO₂ evolution. The sample mass remains stable above 690 °C after a discrete weight loss step corresponding to a relatively sharp CO₂ evolution indicating that the co-precipitate contains substantial amounts of carbonate in addition to hydroxide.



Figure 1. TG-MS: weight loss and MS traces (blue = 18 and green = 44) during heat treatment of the amorphous mixed co-precipitate with 2.5 at % Ru.

Subsequently, the precursor of Ru-2.5 was calcined at different temperatures between 600 and 1000 °C, according to the temperature ranges obtained by TG-MS, to investigate the crystallization and phase evolution. As presented in Figure 2, room temperature XRD shows that the perovskite LaNiO₃ is the main phase already after calcination at 600 °C. Additionally, also very small amounts of crystalline NiO may be present after calcination. With increasing calcination tempera-



Figure 2. XRD – Co-precipitated precursor calcined at different temperatures (heating rate 10 K·min⁻¹) in 21 % O_2/Ar (100 mL·min⁻¹); orange bars: LaNiO₃ (ICDD 79–2541), magenta bars: NiO (ICDD: 47–1049).



ture, the perovskite reflections 024 and 300 around 47 and 58° 2Θ are shifted to smaller angles towards the literature values (Figure 2, inset), indicating ongoing slight modifications of this phase during heating tentatively related to a homogenization at higher temperature.

The formation of low amounts of additional phases upon calcination below 1000 °C was also observed with SEM, where different morphologies can be discerned as shown exemplarily for the sample after calcination at 870 °C (Figure 3a) – images for samples Ru-2.5-600 and Ru-2.5-760 can be found in Figure S4 (Supporting Information). On the other hand, calcination at 1000 °C led to a rather homogeneous shape of the crystallites (Figure 3b). With increasing calcination temperature, the BET surface area is strongly decreased from 25 m²·g⁻¹ (Ru-2.5-600) to 5 m²·g⁻¹ (Ru-2.5-1000).



Figure 3. SEM – morphology of Ru-2.5 after calcination at (a) 870 °C (Ru-2.5-870), (b) 1000 °C (Ru-2.5-1000).

Similar to Ru-2.5, the Ru-free sample Ru-0 was calcined at different temperatures to investigate the influence of Ru. The decomposition of the perovskite LaNiO₃ is described to occur above 980 °C by the formation of RP phases.^[9d] Hence, after calcination at 1000 °C the Ru-free sample Ru-0-1000 is as expected composed of NiO as well as the RP phase La₄Ni₃O₁₀, which has a mixed Ni valence (Figure 4). It has to be noted that after calcination at 760 °C and 870 °C the main phase is LaNiO₃, which is already pre-formed at 600 °C alike in Ru-2.5.

NiLa, pH = 8, calcined with 10Kpm, 21%O₂/Ar (100ml/min)



Figure 4. XRD – Precursor of Ru-0 calcined at different temperatures (heating rate 10 K·min⁻¹) in 21 % O_2 /Ar (100 mL·min⁻¹); orange bars: LaNiO₃ (ICDD 79–2541), magenta bars: NiO (ICDD: 47–1049), green bars: La₄Ni₃O₁₀ (ICDD-79–2541).

Accordingly, the Ru-free sample after calcination at 1000 °C is characterized by different morphologies in SEM (Figure S5a, Supporting Information). Hence, the comparison of Ru-2.5-1000 and Ru-0-1000 shows that Ru incorporation into the precursor has a stabilizing effect on the perovskite structure above its decomposition temperature. Anyway, in this study aiming at high-temperature DRM, the samples are compared after calcination at 1000 °C in the following.

Similar to Ru-2.5-1000, Ru-5-1000 is characterized by a homogeneous morphology (Figure S5b, Supporting Information) and consists only of perovskite phase (Figure S6, Supporting Information). With increase of the Ru content the XRD reflections were slightly shifted to lower angles, i.e. the elementary cell was enlarged as expected for Ru incorporation into the unit cell.

Reduction Behavior

Nickel metal is the active component within the bifunctional catalyst obtained from perovskite, hence, the reduction behavior of Ru-*N*-1000 in flowing hydrogen gas was investigated by temperature-programmed reduction (TPR). As shown in Figure 5 for Ru-2.5-1000, the TPR profile is characterized by at



Figure 5. TPR profile of Ru-2.5-1000 (6 K·min⁻¹). A positive signal in the thermal conductivity detector (TCD) corresponds to a consumption in hydrogen.

least two well-separated peaks. As already mentioned in the Introduction, there are two different descriptions for this behavior in literature by *Gallego* et al.^[7c] and alternatively by *Guo* et al.^[7d] and *Ruckenstein* et al.^[16] proposing either a three-step reduction of LaNiO₃ itself or presence of amorphous NiO, which is claimed to be responsible for the first step.

To clarify this issue and to understand the structural changes upon reduction, we prepared a sample reduced at 440 °C, i.e. at a temperature between the two TPR peaks. Indeed, XRD shows that it still has a perovskitic structure, but a significant change compared to the calcined sample was observed as marked with circles in Figure 6a. The resulting XRD pattern can be refined using the tetragonal oxygen-deficient perovskite La₆Sr₂Cu₈O₂₀ as a proxy structural model in the Rietveld refinement,^[17] as shown in Figure 6b. Taking into account that our catalyst is based on a Ru-doped LaNiO₃ which is subjected to reducing conditions, the new phase is consistent with a partially reduced perovskite "LaNiO_{2.5}",^[14] where Ni is reduced from three-valent to two-valent leading to a stoichiometry analogous to (LaSr)₈Cu₈O₂₀. By such partial reduction the structure itself is changed from orthorhombic to tetragonal, re-



Figure 6. XRD after reduction of Ru-2.5-1000 at 440 °C: (a) comparison with LaNiO₃ (orange bars) and calcined reactant (dashed line) (b) Rietveld refinement using $La_6Sr_2Cu_8O_{20}$ (*P4/mbm*) as structure proxy in stoichiometric agreement with LaNiO_{2.5}.

sulting in the observed perovskitic pattern, which differs from that of $LaNiO_3$ only by the minor peaks encircled in Figure 6a.

Complementary, we used in-situ XRD in hydrogen atmosphere for a detailed investigation of the structural changes during reduction. Therefore, the calcined Ru-2.5-1000 was heated to 200 °C (6 K·min⁻¹), afterwards XRD patterns were measured in steps of 25 °C up to a final temperature of 700 °C. The 2D color plot in Figure 7 shows the changes upon heating in hydrogen (individual patterns are shown in Figure S7, Supporting Information).



Figure 7. In-situ XRD – reduction of NiLaRuO_x (Ru-2.5-1000).

Above 250 °C small thermal changes are observed which may be assigned to a topotactic distortion due to the partial reduction of Ni and/or Ru cations. Once the reduced perovskite phase "LaNiO_{2.5}" is formed around 320 °C, it is stable up to 450 °C, i.e. until onset temperature of the second TPR peak. At 475 °C LaNiO_{3-x} and La₂O₃ are co-existing, as seen by the additional peaks at 22 und 30° 2 Θ . Subsequently, above 475 °C La₂O₃ is formed, indicating a fast reduction of LaNiO_{3-x} in the second TPR step.

The reduction behavior was investigated for the different Ru content and the corresponding TPR profiles are depicted in Figure 8. As shown above, the structure after calcination is



Figure 8. TPR profiles of catalysts after calcination at 1000 °C: Influence of Ru content.

strongly influenced by the presence of Ru, thus explaining the quite different TPR profiles. With higher Ru content (5 at%) the peaks are broadened, i.e. the reduction itself is slowed down. On the other hand, as Ru-0-1000 starts from NiO and the RP phase La₄Ni₃O₁₀ with mixed valent Ni sites, its profile is significantly different. In detail, the first peak is shifted to higher temperatures and is characterized by two distinct shoulders as several steps are occurring in parallel. Anyway, the course of reduction followed by in-situ XRD (Figure 9, individual patterns in Figure S8, Supporting Information) indicates a similar mechanism as for Ru-2.5-1000, i.e. a partially reduced perovskite is formed in between the two reduction peaks, resulting in the structural changes visible around 320 °C. Here, the partially reduced phase is stable up to 400 °C, afterwards some structural fluctuations are followed by the one-step reduction to La_2O_3 .



Figure 9. In-situ XRD - reduction of Ru-0-1000.

Finally, independent of the Ru content and the exact TPR profiles, all three catalysts only contain two phases after reduction – Ni metal and La_2O_3 – as shown in Figure 10. As no



Figure 10. XRD patterns of Ru-0-1000, Ru-2.5-1000 and Ru-5-1000 after reduction at 700 $^{\circ}$ C – formed phases for all three catalysts are Ni and La₂O₃.

separate Ru phase is observed, we assume that Ru-Ni alloys may be formed, which is indicated by the shifted peak position of the Ni 111 reflection near 44° 2 Θ , especially, in reduced Ru-5-1000. It is noted that the thermodynamic solubility of Ru in fcc-Ni is close to zero at room temperature and reaches 5% at 1000 °C. Thus the broad peak near 44° 2 Θ might in fact correspond to the decomposed alloy. Anyway, based on the peak widths of the metallic Ni(Ru) phase, one clear effect of the Ru doping can be seen. Indeed, in absence of Ru the formed Ni phase is much more crystalline with sharper peaks (top pattern in Figure 10) than in the Ru-doped Ni/La₂O₃ catalysts. This peak broadening effect might be related to a higher dispersion of the metallic phase.

The reductive decomposition of the perovskite precursor and the corresponding evolution of the catalyst's microstructure were additionally investigated by high resolution transmission electron microscopy (HR-TEM) for Ru-2.5. Figure 11a shows an HRTEM image of the calcined pre-catalyst Ru-2.5-1000. A large crystalline particle exhibiting the perovskite structure can be seen. Comparison with the state after reduction at 700 °C



Figure 11. HR-TEM images of Ru-2.5-1000 before (top) and after (bottom) reduction in hydrogen at 700 $^{\circ}$ C.

as shown in Figure 11b confirms that the perovskite was decomposed. The large particles have transformed into aggregates of crystalline, but substantially smaller domains of random orientation due to the segregation of La_2O_3 and Ni upon reduction.

Catalytic Performance in DRM

The Ni(Ru)/La₂O₃ catalysts obtained from reduction of the perovskite precursors were tested for their catalytic activity in DRM at 950 °C in a CH_4/CO_2 gas mixture (19% CH_4 , 24% CO_2 in Ar). Beforehand, the calcined catalysts were activated by reduction in the reactor in diluted hydrogen at 700 °C (5 K·min⁻¹, 4% H₂/Ar).

Figure 12a shows the methane consumption rate as a function of time-on-stream. Due to the high reaction temperature, all three catalysts are characterized by quite high rates. Despite the pre-reduction, an activation period was observed within the first 3–10 h of DRM for all catalysts. This indicates that the active surface of this system is only formed under operating DRM conditions and is at least partly ascribed to transformations of the active Ni phase between reduction (700 °C) and reaction temperature (950 °C). After the activation period a



Figure 12. Dry reforming of perovskite-derived Ni(Ru)/La₂O₃ catalysts with different Ru content: (a) activity: integral reaction rate of CH₄ conversion at 950 °C, (b) coking behavior: oxygen consumption in subsequent TPO.

quite significant deactivation was observed. The comparison of the three catalysts shows that due to the presence of Ru the activity increased by a factor of 1.5–2. Surprisingly, the Ru-5 catalyst performs rather similar to the Ru-free one and is clearly inferior to Ru-2.5.

As all Ni catalysts are sensitive to the formation of carbonaceous species during DRM,^[18] we investigated the coking behavior with a subsequent temperature-programmed oxidation (TPO). The amounts of oxygen consumed for oxidizing the carbonaceous deposits are presented in Figure 12b. Indeed, with Ru present in the catalyst, significantly less carbon is formed during DRM as seen by the lower oxygen consumption.

Conclusions

A constant pH co-precipitation for the synthesis of LaNiO₃ perovskite precursors was successfully applied. The introduction of Ru has a stabilizing effect on the perovskite structure upon calcination and hinders the decomposition into NiO and RP phases at high temperatures. Furthermore, the reduction mechanism of the orthorhombic LaNiO₃ precursors was unveiled. First a partial reduction occurs resulting in formation of a sub-stoichiometric LaNiO2.5 intermediate with a tetragonal structure. Subsequently, the partially reduced perovskite undergoes a one-step reduction to form Ni metal in a La₂O₃ matrix. The catalytic application in DRM indicates that addition of 2.5 at % of Ru has a promoting effect likely due to stabilization of the metallic Ni phase. The promoting effect was absent for the Ru-free catalyst and strongly decreased upon addition of higher Ru amounts (5%). Anyway, as expected, the addition of Ru led to a successful mitigation, yet not complete suppression of carbonaceous deposits.

Experimental Section

Catalyst Preparation: The catalysts were prepared by constant pHcontrolled co-precipitation in an automated laboratory reactor (Mettler-Toledo Labmax) at 25 °C from a 0.385 M aqueous solution of solution of Na₂CO₃, and a 0.245 M aqueous solution of the metal salts [La(NO₃)₂. 6 H₂O, Ni(NO₃)₂·6 H₂O, RuCl₃·xH₂O] at pH 8. The amount of ruthenium was varied between 0-5 at %. The molar La:(Ni+Ru) ratio was fixed at 1:1. The metal salt solutions and the precipitating agent were added simultaneously to keep the pH value constant. After subsequent ageing and washing the samples were dried for ca. 16 h at 110 °C. The samples are labeled in the following according to the Ru content as Ru-0, Ru-2.5 and Ru-5. For structural and morphological investigation these precursors were calcined at different temperatures (each 10 K·min⁻¹) in 21 % O₂/Ar (100 mL·min⁻¹). The calcined samples are denoted Ru-N-T with N corresponding to the Ru content and T to the calcination temperature in °C. For further investigation of the reduction behavior and catalytic performance the samples were calcined for 5 h at 1000 °C (10 K·min⁻¹) in 21 % O₂/Ar (100 mL·min⁻¹) – labeled as Ru-N-1000. All calcinations were performed in a tubular furnace (Carbolite) equipped with a ceramic tube (corundum) and mass flow controllers (Bronkhorst) for defined gas flow and composition.

Catalyst Characterization: The elemental composition of the calcined catalysts was examined by wavelength dispersive X-ray fluores-

cence (WDXRF) using a Sequential Pioneer S4 Spectrometer (Bruker), where the K lines were analyzed. X-ray diffraction (XRD) patterns were recorded with a STOE Stadi-P diffractometer in transmission geometry using Cu- $K_{\alpha 1}$ radiation, a primary Ge monochromator and a 6° linear position sensitive detector. Simultaneous thermogravimetry and differential scanning calorimetry (TG-DSC) was carried out with a Netzsch STA449 Jupiter thermoanalyzer (2 K·min⁻¹, synthetic air), equipped with an electromagnetic microbalance with top loading. The gas phase analysis during TG-DCS was monitored with a quadrupole mass spectrometer (Pfeiffer, OMS200 Thermostar) coupled with STA thermobalance via quartz capillary. Evolution of water and carbon dioxide was recorded by monitoring the change of intensity of the ion currents of OH⁺, H₂O⁺, CO⁺, and CO₂⁺ (m/z = 17, 18, 28, 44). SEM images were taken in a Hitachi S-4800 (FEG) system. The BET surface areas were determined by measuring the nitrogen adsorption-desorption isotherms with a Quantachrome Autosorb automatic BETsorptometer at -196 °C with nitrogen as the analysis gas. Prior to the analysis, the samples were outgassed for 2 h at 100 °C. The reduction behavior was investigated by temperature programmed reduction (TPR) in 5 vol% H₂ in Ar with a flow of 80 mL·min⁻¹ up to 350 °C using a fixed bed reactor (TPDRO-1100, CE instruments). The H₂ consumption was monitored with a thermal conductivity detector (TCD). In agreement with the suggestions of Monti and Baiker^[19] and Malet and Caballero^[20] a heating rate of 6 K·min⁻¹ was used. The microstructure of the samples was examined by using Philips CM200 transmission electron microscopes (TEM) equipped with a LaB₆ cathode or a field electron gun. High-resolution images were taken with a CCD camera. Both samples were dispersed in chloroform and deposited on a holey carbon film supported on a copper grid. For the investigation of the microstructure of the reduced catalyst, the sample was reduced and subsequently passivated by slow increase of oxygen partial pressure at room temperature prior to transfer into the microscope.

Dry Reforming of Methane: The catalytic experiments in DRM were performed in a continuous flow system at atmospheric pressure using a fixed-bed tubular quartz reactor of 8 mm inner diameter. The reactor was equipped with a ceramic tube in the radial center of the reactor to measure the temperature at the sample position. A calibrated on-line GC analysis (Shimadzu 14-B) was used to analyze the product gas composition. For transient studies a coupled IR-detector (CO, CO2 and CH₄) with a TCD for H₂ (Emerson MLT4 multi-channel analyzer) and a paramagnetic O₂ detector (Magnos 16) were used. For the catalytic test, 0.5 mg of the calcined catalyst (sieve fraction of 250–355 µm) was diluted with 490 mg of high purity SiC (sieve fraction of 125-180 μ m). Initially, the catalyst was activated by reduction at 700 °C in $4\,\%$ H_2/Ar (99.9 %/99.99 %) and a total flow of 20 NmL·min^-1 with a linear heating rate of 5 K min-1. Afterwards, the catalyst was heated in argon (99.999%) to the aspired reaction temperature of 950 °C. The dry reforming reaction was carried out for 60h using a gas mixture of $19\,\%$ CH_4 (99.9995 %) and $24\,\%$ CO_2 (99.9995 %) in argon, the total flow was set to 230 NmL·min⁻¹. To ensure a CO_2/CH_4 ratio > 1:25 at any time, the CH₄ partial pressure was increased stepwise while starting the experiment. After cooling to room temperature, a subsequent TPO experiment was performed with a flow rate of 100 NmL·min⁻¹ of 4.5% O2/Ar (99.995%/99.999%) and a linear heating rate of 5 K·min⁻¹. The final temperature of 950 °C was held constant until no more O₂ consumption was observed.

Supporting Information (see footnote on the first page of this article): contains a protocol of the co-precipitation synthesis as well as additional characterization data as mentioned in the text above.

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References

- [1] M. C. J. Bradford, M. A. Vannice, *Catal. Rev. Sci. Eng.* **1999**, *41*, 1–42.
- [2] S. Wang, G. Q. Lu, *Energy Fuels* **1996**, *10*, 896–904.
- [3] H. S. Bengaard, J. K. Nørskov, J. Sehested, B. S. Clausen, L. P. Nielsen, A. M. Molenbroek, J. R. Rostrup-Nielsen, J. Catal. 2002, 209, 365–384.
- [4] H. Cheng, S. Feng, W. Tao, X. Lu, W. Yao, G. Li, Z. Zhou, Int. J. Hydrogen Energy 2014, 39, 12604–12612.
- [5] L. Mo, K. K. M. Leong, S. Kawi, *Catal. Sci. Technol.* 2014, 4, 2107–2114.
- [6] M. A. Pena, J. L. G. Fierro, Chem. Rev. 2001, 101, 1981–2017.
- [7] a) G. C. de Araujo, S. de Lima, J. M. Assaf, M. A. Pena, J. L. Garcia Fierro, M. d. C. Rangel, *Catal. Today* 2008, *133–135*, 129–135; b) G. S. Gallego, C. Batiot-Dupeyrat, J. Barrault, F. Mondragón, *Ind. Eng. Chem. Res.* 2008, *47*, 9272–9278; c) G. S. Gallego, F. Mondragón, J. Barrault, J.-M. Tatibouet, C. Batiot-Dupeyrat, *Appl. Catal. A: General* 2006, *311*, 164–171; d) J. Guo, H. Lou, Y. Zhu, X. Zheng, *Mater. Lett.* 2003, *57*, 4450–4455; e) V. R. Choudhary, B. S. Uphade, A. A. Belhekar, *J. Catal.* 1996, *163*, 312–318; f) C. Batiot-Dupeyrat, in *Perovskites and Related Mixed Oxides*, Wiley-VCH, Weinheim, 2016, pp. 501–516.
- [8] a) S. N. Ruddlesden, P. Popper, *Acta Crystallogr.* 1957, 10, 538– 539; b) S. N. Ruddlesden, P. Popper, *Acta Crystallogr.* 1958, 11, 54–55.
- [9] a) M. Zinkevich, F. Aldinger, J. Alloys Compd. 2004, 375, 147–161; b) M. Zinkevich, N. Solak, H. Nitsche, M. Ahrens, F. Aldinger, J. Alloys Compd. 2007, 438, 92–99; c) D. O. Bannikov, A. P. Safronov, V. A. Cherepanov, Thermochim. Acta 2006, 451, 22–26; d) D. O. Bannikov, V. A. Cherepanov, J. Solid State Chem. 2006, 179, 2721–2727.
- [10] M. M. Nair, S. Kaliaguine, in *Perovskites and Related Mixed Oxides*, Wiley-VCH Verlag, Weinheim, **2016**, pp. 47–68.
- [11] J. D. G. Fernandes, D. M. A. Melo, L. B. Zinner, C. M. Salustiano, Z. R. Silva, A. E. Martinelli, M. Cerqueira, C. Alves Júnior, E. Longo, M. I. B. Bernardi, *Mater. Lett.* **2002**, *53*, 122–125.
- [12] X. Weng, P. Boldrin, I. Abrahams, S. J. Skinner, S. Kellici, J. A. Darr, J. Solid State Chem. 2008, 181, 1123–1132.
- [13] R. Pereñiguez, V. M. Gonzalez-delaCruz, A. Caballero, J. P. Holgado, Appl. Catal B: Environ. 2012, 123, 324–332.
- [14] S. Singh, D. Zubenko, B. A. Rosen, ACS Catal. 2016, 6, 4199– 4205.
- [15] a) K. Mette, S. Kühl, H. Düdder, K. Kähler, A. Tarasov, M. Muhler, M. Behrens, *ChemCatChem* 2014, 6, 100–104; b) K. Mette, S. Kühl, A. Tarasov, M. G. Willinger, J. Kröhnert, S. Wrabetz, A. Trunschke, M. Scherzer, F. Girgsdies, H. Düdder, K. Kähler, K. F. Ortega, M. Muhler, R. Schlögl, M. Behrens, T. Lunkenbein, *ACS Catal.* 2016, 6, 7238–7248.
- [16] E. Ruckenstein, Y. H. Hu, J. Catal. 1996, 161, 55-61.

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- [17] a) R. Genouel, C. Michel, B. Raveau, *Chem. Mater.* 1995, 7, 2181–2184; b) H. Yamaguchi, H. Matsuhata, T. Ito, K. Oka, *Physica C: Superconductivity* 1997, 282, 1079–1080.
- [18] H. Düdder, K. Kähler, B. Krause, K. Mette, S. Kühl, M. Behrens, V. Scherer, M. Muhler, *Catal. Sci. Technol.* 2014, *4*, 3317–3328.
 [10] D. A. M. Monti, A. Beiler, J. Catal. 1002, 832 2022 225
- [19] D. A. M. Monti, A. Baiker, J. Catal. 1983, 83, 323-335.
- [20] P. Malet, A. Caballero, J. Chem. Soc. Faraday Trans. I 1988, 84, 2369–2375.

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