Bi-functional Ru/Ca$_3$Al$_2$O$_6$–CaO catalyst–CO$_2$ sorbent for the production of high purity hydrogen via sorption-enhanced steam methane reforming†

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Sorption-enhanced steam methane reforming (SE-SMR) combines steam methane reforming and a CO$_2$ abstraction reaction to yield high purity hydrogen. In this work, we report on the development of a bi-functional catalyst–sorbent containing Ru as the reforming catalyst and CaO as the solid CO$_2$ sorbent via a citrate sol–gel route. The material contains CaO, a structural stabilizer (Ca$_3$Al$_2$O$_6$) and Ru nanoparticles (~5 nm, 3 wt%) that are formed upon reduction in H$_2$. This new material was found to outperform significantly the benchmarks Ni–CaO and Ru/limestone in terms of yield of high-purity hydrogen and coke resistance. Using highly active Ru nanoparticles for the SMR allowed to maximize the weight fraction of the CO$_2$ sorbent CaO, hence increasing significantly the CO$_2$ capture capacity of the material. This favorable characteristic of the material led to an appreciably extended pre-breakthrough duration. In addition, we demonstrate that the material developed was very stable over multiple SE-SMR/regeneration cycles. The excellent cyclic stability is ascribed to the presence of Ca$_3$Al$_2$O$_6$ that stabilized effectively the porous structure of the material against sintering.

1. Introduction

Hydrogen is a carbon-free energy carrier that features a high energy density (120–142 MJ kg$^{-1}$).1,2 In addition, hydrogen is also an important chemical feedstock for a number of large scale processes such as ammonia synthesis or the refining of crude oil.3 Although its combustion does not yield any CO$_2$ emissions, the large scale processes through which it is currently produced, e.g. the steam reforming of natural gas (SMR), are energy intensive and emit large quantities of CO$_2$ as a side product.4 For example, the conventional SMR process (CH$_4$ + H$_2$O ^= 3H$_2$ + CO, $\Delta H_{298}^0$ = 206 kJ mol$^{-1}$) produces 7 kg CO$_2$ per kg H$_2$.5 Besides the emission of CO$_2$, SMR is also an equilibrium limited process, i.e. at the SMR working a gas mixture containing approximately 76% H$_2$, 17% CO$_2$, 3% CO and 4% CH$_4$ is obtained.6,7 CO is converted further with steam via the water gas shift reaction (CO + H$_2$O ^= CO$_2$ + H$_2$, $\Delta H_{298}^0$ = −41 kJ mol$^{-1}$) to CO$_2$, yielding an additional mole of H$_2$ per mole CO. Unconverted CO (after the high and low temperature WGS steps) is selectively oxidized to CO$_2$ which is subsequently removed from the hydrogen stream by pressure swing adsorption (PSA) or amine scrubbing.8

The sorption-enhanced steam methane reforming (SE-SMR: CH$_4$ + 2H$_2$O + sorbent ^= sorbent–CO$_2$ + 4H$_2$) is a promising approach to overcome the drawbacks of the traditional SMR.9 In this process the SMR and WGS reactions proceed in the presence of a solid CO$_2$ sorbent. The abstraction of the product CO$_2$ shifts the equilibrium to the product side (Le Chatelier’s principle) yielding high-purity H$_2$ in a single step. This allows the SE-SMR reaction to be operated also at a lower temperature of ≈550 °C compared to the conventional SMR (800–1000 °C), potentially reducing the rate of catalyst deactivation by thermal sintering.

A key component of the SE-SMR process is a CO$_2$ sorbent that should possess a high CO$_2$ uptake in the temperature range of interest (500–900 °C). In this context, CaO is a promising candidate due to (i) its high theoretical CO$_2$ uptake (0.78 g CO$_2$/g sorbent), (ii) the high abundance of its natural precursors, e.g., limestone, (iii) its low CO$_2$ capture costs ($9–11$ per ton of CO$_2$ captured),10 and (iv) its fast kinetics for CO$_2$ uptake and release (CaO + CO$_2$ ^= CaCO$_3$, $\Delta H_{298}^0$ = −178 kJ mol$^{-1}$). It is important to note that the incorporation of a
CaO-based CO₂ abstraction reaction turns the highly endothermic SMR reaction into an exothermic reaction (CH₄ + 2H₂O + CaO \rightleftharpoons H₂ + CaCO₃, ΔH²⁹₈\text{K} = -13 \text{ kJ mol}^{-1}).

However, the cyclic performance of CaO-based CO₂ sorbents is hampered by the low Tammann temperature of CaCO₃ (Tₚ \approx 530 °C) leading to sintering and in turn a loss in porosity. A high porosity is, however, required as the molar volume of the reaction product (CaCO₃) is almost twice as high as that of the reactant (CaO).\textsuperscript{11,12} Therefore, to avoid that the CO₂ uptake proceeds in a slow, diffusion-limited regime (the diffusivity of CO₂ in CaCO₃, D_{CaCO₃} = 0.003 \text{ cm}² \text{ s}^{-1}, is two orders of magnitude lower than that in CaO, D_{CaO} = 0.3 \text{ cm}² \text{ s}^{-1}), a high porosity of the sorbent is critical. To counteract sintering, attempts have been made to stabilize the CaCO₃/CaO structure with high Tammann temperature metal oxides such as Al₂O₃, MgO, TiO₂, SiO₂, and ZrO₂.\textsuperscript{13-16} As the reaction becomes diffusion-limited at a CaCO₃ thickness of \sim 50 nm,\textsuperscript{17} also nano-structuring of the sorbent becomes an important aspect to minimize diffusion lengths.

Besides requiring a solid CO₂ sorbent, the SE-SMR relies on a SMR catalyst, typically a transition metal such as Pt, Ru, Rh, Pd, Ir, Co or Ni.\textsuperscript{18} An additional requirement for the catalyst in the SE-SMR process is its stability in cyclic SE-SMR-regeneration. Conceptually, it is possible to simply mix a SMR catalyst with a CO₂ sorbent. However, the availability of a bi-functional material that contains both the CO₂ sorbent and the catalyst would have a number of advantages, such as enhancing heat and mass transfer and reducing the quantity of inactive support.\textsuperscript{19,20} However, the design and manufacture of highly active and stable bi-functional materials is challenging as there is a potential for an irreversible interaction (e.g. formation of inactive solid solutions) between the CO₂ sorbent, the catalyst and the support.\textsuperscript{21-23} In addition, material migration during CO₂ uptake and regeneration may block the active sites of the catalyst. In order to overcome the sintering-induced deactivation, approaches that incorporate an structural stabilizer such as Mg₆Al₇O₁₆,\textsuperscript{24} Ca₃(PO₄)₂,\textsuperscript{25} Ca₁₂Al₁₆O₄₃,\textsuperscript{26-29} Ca₉Al₆O₁₈,\textsuperscript{30} Ca₅Al₆O₁₄,\textsuperscript{31} Ca₅Al₂O₆ (ref. 32) have been applied to develop more effective bi-functional catalyst–sorbents. However, high metal loadings of the catalyst (15–50 wt% Ni or Co)\textsuperscript{24,25,33} have been typically required to obtain materials with acceptable SMR activity. However, such high catalyst loadings lead to a reduced CO₂ uptake capacity per gram of material, thus, affecting negatively the economics of the SE-SMR process.

In this work, we report the development of a bi-functional material that contains Ru as the reforming catalyst and CaO as the solid CO₂ sorbent. The materials were synthesized \textit{via} a scalable, one-pot synthesis route (citrate sol-gel method). The synthesized materials (Ru/CaO and Ru/Ca₅Al₂O₆-CaO) were compared to the following benchmark materials: Ru impregnated on limestone-derived CaO (Ru/lime) and a bi-functional Ni-based material (Ca–Ni-ex-Htlc).\textsuperscript{24} The SE-SMR performance of the synthesized bi-functional materials was tested at 550 °C under equilibrium limitations (8.4 L g\textsubscript{cat}⁻¹ h⁻¹ of GHSV, CH₄:H₂O:N₂ = 1:4:9). The yield of high purity hydrogen was evaluated over ten repeated cycles of SE-SMR and regeneration (at 750 °C). The stability of the materials for SE-SMR was also determined under kinetic control at 550 °C (84 L g\textsubscript{cat}⁻¹ h⁻¹ of GHSV, CH₄:H₂O:N₂ = 1:4:9). The bi-functional material Ru/Ca₅Al₂O₆ yielded a remarkable quantity of high purity hydrogen (12–13 mmol) in the pre-breakthrough regime, outperforming the benchmark Ca–Ni-ex-Htlc and Ru/lime by more than 590%. Differences in the SE-SMR performance of the materials tested, are discussed in view of a detailed characterization of the as-synthesized and reacted materials using X-ray absorption spectroscopy (XAS), electron microscopy, X-ray powder diffraction (XRD) and N₂ physisorption.

2. Experimental

2.1. Material preparation

2.1.1. Bi-functional catalyst–sorbent. Two bi-functional Ru and CaO containing materials, referred to in the manuscript as Ru/CaO and Ru/Ca₅Al₂O₆-CaO, were synthesized by a citrate sol-gel route.\textsuperscript{34} Here, citric acid (50 mmol) and ethylene glycol (30 mmol) were dissolved in 100 ml of deionized water. Subsequently calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O, Acros Organics), ruthenium nitrosyl nitrate (Ru(NO)(NO₃)₂, Acros Organics) and (only in the case of Ru/Ca₅Al₂O₆-CaO) aluminium nitrate nonahydrate (Al(NO₃)₃·9H₂O, Acros Organics) were added in stoichiometric amount (total 10 mmol of metal precursors). The weight fraction of Ru was 3 wt% in both materials, and the molar ratio of Ca²⁺:Al²⁺ in Ru/Ca₅Al₂O₆-CaO was 9:1 (as determined by ICP-OES). The solution was heated up to 110 °C under vigorous stirring until gel formation occurred. This was followed by drying at 130 °C in an oven. Subsequently, the dried materials were calcined at 850 °C (5 °C min⁻¹ heating rate) for 2 h and sequentially ground and sieved to 100–300 μm. The bi-functional Ru/lime (3 wt% Ru) was prepared by wet impregnation. 1 g of Rheinkalk limestone calcined at 800 °C was added to 100 ml of an aqueous solution of ruthenium nitrosyl nitrate (3.0 mM) under vigorous stirring for 5 h. The water was evaporated subsequently in a rotary evaporator (Heidolph) at 80 °C (300 mbar). The materials were dried at 110 °C in an oven overnight, followed by calcination at 850 °C. A bi-functional material containing a Ni catalyst (45 wt% Ni, Ca–Ni-ex-Htlc) was prepared by co-precipitation and contained the following phases (after calcination): NiO, CaO and MgAl₂O₄. Details of its physical–chemical properties have been reported elsewhere.\textsuperscript{24}

2.1.2. Reference materials for structural characterization. In order to provide a better understanding of the bi-functional Ru–CaO catalysts, the following reference materials were prepared for XAS and H₂-TPR measurements: (i) CaRuO₃ (exhibiting a perovskite structure) was prepared by a citrate sol-gel route using ruthenium nitrosyl nitrate and calcium nitrate (1:1 molar ratio; in total 10 mmol of metal precursors), and (ii) Ru (3 wt%) supported on γ-Al₂O₃ (Alfa Aesar) was prepared by impregnation using
Ru(NO)(NO3)3 (Acros Organics) and it is referred as Ru/Al2O3. The reference materials were calcined at 850 °C (5 °C min⁻¹) for 2 h. Additionally, RuO2 (Sigma-Aldrich) with a rutile structure was used as a reference material.

2.2. Material characterization

The elemental composition of the calcined materials was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 5100 VDV). The surface area and pore volume of the freshly calcined and reacted materials were determined using a Quantachrome (NOVA 4000e) N2 adsorption analyzer. Prior to N2 adsorption, each sample was degassed at 250 °C for 3 h under vacuum (10⁻³ mbar). The Brunauer et al. (BET)¹⁵ and the Barrett et al. (BJH) models³⁶ were used to calculate the surface area and pore size distribution, respectively.

Temperature-programmed reduction in H₂ (H₂-TPR) was conducted in an Autochem 2920 equipped with a thermal conductivity detector. For these measurements, 30–50 mg of the calcined catalyst was placed in a quartz reactor and heated to 300 °C in an argon atmosphere (50 mL min⁻¹) to dehydrate the sample. Next, the materials were cooled down to 50 °C and the gas was switched to 5 vol% H₂/Ar (50 mL min⁻¹). Subsequently, the temperature was increased at a rate of 5 °C min⁻¹.

Temperature-programmed oxidation (TPO) was used to determine the quantity of coke deposited on the spent catalyst. TPO experiments were performed in a thermogravimetric analyzer (TGA, Mettler Toledo TGA/DSC 3). Here, approximately 20 mg of the spent catalyst was loaded into an alumina crucible. Prior to TPO, the sample was heated to 100 °C with a heating rate of 10 °C min⁻¹ in 100 mL min⁻¹ of air. After a holding time of 1 h, the sample was heated further to 1000 °C (10 °C min⁻¹ in 100 mL min⁻¹ of air). The weight loss of the sample was continuously recorded and used to determine the mass of coke deposited.

H₂ chemisorption was carried out in an Autochem 2920 apparatus. 50–60 mg of a material was reduced in a quartz reactor at 500 °C for 1 h in 5 vol% H₂/Ar (50 mL min⁻¹). The sample was then cooled down to 400 °C and purged with Ar (50 mL min⁻¹) for 30 min. After cooling down further to 50 °C in Ar, the quantity of chemisorbed H₂ was determined by repeatedly injecting pulses of 5 vol% H₂/Ar into the reduced catalyst bed. The stoichiometry factor of dissociated H₂ to Ru was set to 1.0 (H/Ru).³⁷–³⁹

The crystalline phases in the materials were studied using an Empyrean (PANalytical) powder X-ray diffractometer operated at 40 mA and 40 kV using Cu Ka (λ = 0.1541 nm) radiation. The diffraction patterns were recorded in the range 2θ = 5–90° with 0.016° of step size.

The morphology of the samples was studied by electron microscopy (viz. scanning electron microscopy, SEM, FEI Magellan 400 FEG, transmission electron microscopy, TEM, Philips CM12 and FEI Talos F200X and a scanning transmission electron microscopy, STEM, Hitachi HD-2700) equipped also with an energy-dispersive X-ray (EDX) detector.

**In situ** X-ray absorption spectroscopy (XAS) experiments (Ru K-edge, 22.1 keV) were performed at the Swiss-Norwegian Beamlines (SNBL, BM31) of the European Synchrotron Radiation Facility (ESRF). Here, the calcined material, approximately 2 mg, was loaded in a capillary quartz reactor (1.0 mm of outer diameter) and heated up to 500 °C, with a ramp rate of 10 °C min⁻¹ in 5 vol% H₂/He (10 ml min⁻¹). Ex situ XAS measurement were also performed on the as-synthesized materials (bi-functional materials and references). The materials were mixed with cellulose (ratio chosen such that XAS measurements in transmission mode were optimized) and ground to a fine powder. The pelletized samples were measured in transmission mode. XAS spectra were collected at the Ru K-edge using a double-crystal Si (111) monochromator (continuous scanning mode) and the data were analyzed using the Athena and Arthemis software.⁴⁰

2.3. Cyclic CO₂ capture experiments

Cyclic CO₂ capture and regeneration experiments were performed in a TGA (Mettler Toledo TGA/DSC 3). Approximately 10 mg of the calcined material were heated to 900 °C at a heating rate of 50 °C min⁻¹ under a flow of N₂ (total flow rate of 120 mL min⁻¹ including a constant purge flow of N₂, 25 mL min⁻¹, over the microbalance). When the temperature of 900 °C was reached a holding time of 4 min was applied to ensure complete calcination. This was followed by a reduction of the temperature to 650 °C. At 650 °C, the CO₂ capture step was performed (20 min under 20 vol% of CO₂ in N₂ total flow rate: 150 ml min⁻¹). After carbonation, the CO₂ sorbent was regenerated at 900 °C for 10 min in a CO₂ atmosphere (30 mL min⁻¹). 10 cycles of repeated carbonation and calcination steps were performed.

The cyclic CO₂ capture performance was tested further under SE-SMR-mimicking conditions (carbonation: 550 °C using 50 ml min⁻¹ of 20% CO₂/N₂, 2 h, and regeneration: 750 °C, 50 ml min⁻¹ of N₂, 15 min). Prior to CO₂ capture, the calcined material was heated to 800 °C (10 °C min⁻¹) under N₂ (50 ml min⁻¹) followed by reduction at 500 °C (10 °C min⁻¹) for 2 h in 10 vol% H₂/N₂ (50 ml min⁻¹). Ten repeated cycles of carbonation (550 °C, 50 ml min⁻¹ of 20 vol% CO₂/N₂) and regeneration (750 °C, 50 ml min⁻¹ of N₂) were performed.

2.4. Cyclic SE-SMR experiments

The cyclic SE-SMR reaction was carried out in a fixed-bed quartz reactor (12.6 mm internal diameter and 400 mm length). 100 mg of the calcined bi-functional material (diluted with SiC with a weight ratio of 1:10) was used. Prior to the activity test, the bed was heated up to 800 °C (10 °C min⁻¹). A holding time of 1 h (N₂ with 100 mL min⁻¹) ensured the complete calcination of CaCO₃ to CaO. Subsequently, the bed temperature was reduced to 500 °C. At 500 °C the bed was treated for 2 h in 10 vol% H₂/N₂ (100 mL min⁻¹). After reduction, the SE-SMR was performed at 550 °C using a total flow rate of 14 mL min⁻¹ (8.4 L gcat⁻¹ h⁻¹ of GHSV and CH₄:+H₂O:N₂ = 1:4:9). After 2 h of the SE-SMR,
the bed was heated up to 750 °C (20 °C min⁻¹) in N₂ (50 ml min⁻¹) for regeneration (15 min). In total 10 cycles of SEMR/regeneration were performed. The composition of the off-gas (after condensation of unreacted steam) was analyzed using a micro-GC (C2V-200, Thermo Scientific) equipped with a thermal conductivity detector (TCD) and molecular sieve 5A and U-plot column cartridges.

3. Results and discussion
3.1. Physical–chemical and textural properties
The elemental composition determined by ICP-OES and the textural characteristics of the Ru–CaO-based materials (Ru/CaO, Ru/Ca₃Al₂O₆–CaO and Ru/lime) after calcination (850 °C in air) and reduction (500 °C under 10 vol% H₂/N₂) are summarized in Table 1. The elemental composition of the calcined catalysts shows a very similar loading of Ru in the materials studied here (1.6–1.7 mol% corresponding to 2.8–2.9 wt%) and is in good agreement with the desired composition. The N₂ isotherms of all of the calcined materials tested is feature relatively broad peaks of CaO, characteristic of a nanostructured material. Indeed, the average crystallite sizes of CaO, calculated by the Scherrer equation,⁴¹ are ~36 nm and ~27 nm for Ru/CaO and Ru/Ca₃Al₂O₆–CaO, respectively (Table 1). These values are considerably smaller than that determined for Ru/lime (~70 nm). In addition, for all of the calcined, Ru–CaO containing materials we observe additional, weak peaks that are likely due to the presence of a perovskite CaRuO₃ phase (Pnma space group, inset in Fig. 1a). However, due to the low intensity of these peaks (low Ru loading) and the overlap with other phases present, XRD provides only limited information of the Ru containing phases. Therefore, the materials were characterized further by Ru K-edge XAS to understand better the local environment of Ru after calcination and reduction (Fig. 1b) and in particular the interaction with the CO₂ capture active phase CaO.

For XAS analysis, the following reference materials were measured, and also characterized by XRD (Fig. S3†) prior to XAS analysis: (i) bulk (rutile) RuO₂ and (ii) CaRuO₃, which contains a pure orthorhombic perovskite phase (Pnma space group). In CaRuO₃, Ru is in an octahedral coordination, and in rutile RuO₂ in an axially elongated octahedral coordination. The X-ray absorption near edge structure (XANES) measurements acquired (Fig. 1b) show very distinct features for the CaRuO₃ and RuO₂ references. Both RuO₂ and CaRuO₃ compounds exhibit two peaks: at 22.136 and 22.149 eV, with the latter being more intense for CaRuO₃. Additionally, CaRuO₃ exhibits a feature at 22.178 eV which is absent in RuO₂. Owing to these features in the XANES signal we can distinguish between a RuO₂ or CaRuO₃-like local environment of Ru. For instance, in agreement with XRD, the Ru/Al₂O₃ reference shows the same XANES features as RuO₂. Turning to the bi-functional materials, the presence of features at 22.149 and 22.178 eV in Ru/lime, Ru/CaO and Ru/ Ca₃Al₂O₆–CaO indicates that in these materials Ru is in a CaRuO₃-like local environment. To provide further insight into the local environment of Ru in the calcined materials, the extended X-ray absorption fine structure (EXAFS) data of the CaRuO₃ reference, Ru/lime, Ru/CaO and Ru/Ca₃Al₂O₆–CaO were fitted (Table S1 and Fig. S4†). In line with the atomic arrangement of a CaRuO₃ perovskite according to crystallographic data,⁵² the CaRuO₃ reference data were fitted with a Ru–O shell at 2.0 Å, four Ru–Ca shells with

### Table 1 Physical–chemical properties of the bi-functional Ru–CaO catalysts–sorbents

| Material     | Ru [mol%] | Ca [mol%] | Al [mol%] | N₂ physisorption | Crystallite size [nm] | Ru particle size [nm] | H₂ uptake [µmolRu·h⁻¹] |
|--------------|-----------|-----------|-----------|------------------|----------------------|----------------------|-----------------------|
| Ru/lime      | 1.7       | 97.3      | —         | 12               | 0.11                 | 70                   | 22.6 ± 2.6             |
| Ru/CaO       | 1.6       | 98.4      | —         | 17               | 0.19                 | 36                   | 11.2 ± 2.2             |
| Ru/Ca₃Al₂O₆–CaO | 1.7           | 88.6       | 9.7       | 23               | 0.26                 | 27                   | 5.3 ± 1.3              |

a The bi-functional Ru–CaO catalyst–sorbent was calcined at 800 °C in static air and reduced in 10 vol% H₂/N₂. b The normalized metal mol% of Ru, Ca and Al in the calcined materials were obtained by ICP-OES. c Textural properties of the calcined materials. d Average crystallite size of CaO and Ru (in the reduced materials) determined by TEM. e The quantity of surface Ru in the reduced materials as determined by H₂ chemisorption using a stoichiometry factor of 1.0 of H/Ru,⁵⁷–⁵⁹ parenthesis represents Ru dispersion (%) in the reduced catalysts.
interatomic distances in the range of 3.14–3.61 Å and one Ru–Ru shell at 3.84 Å (and with coordination numbers set to the crystallographic values). The same model of the local structure of Ru was applied to Ru/lime, Ru/CaO and Ru/Ca3Al2O6–CaO. All three Ru–CaO-based sorbents showed a Ru–O coordination sphere at interatomic distances in the range of 1.95–1.97 Å, four Ru–Ca shells with interatomic distances in the range of 3.10–3.47 Å and a Ru–Ru shell at 3.76–3.87 Å. These results are in line with the XANES observation that suggests Ru has a local environment consistent with CaRuO3. On the other hand, the Debye Waller factors observed for the synthetic materials were larger than for the reference crystalline perovskite. This can be explained by a higher disorder of the local environmental of Ru in a highly dispersed CaRuO3-phase within the CaO or CaO–Ca3Al2O6 matrix.

The reduction characteristics of the different materials (bi-functional materials and references) were assessed by H2-TPR experiments (Fig. 1c) after calcination (in air) at 800 °C. The diffractogram of the calcined materials (Fig. 1a) confirmed that there was no CaCO3 in the samples. In addition, all H2-TPR profiles showed a stable baseline between 600–1000 °C (without any further H2 consumption). The TPR profile of the reference bulk RuO2 shows a reduction peak at 130 °C, in agreement with literature.43 On the other hand, Ru/Al2O3 show higher reduction temperatures, viz. 239 °C. In agreement with literature.44,45 The reference CaRuO3 shows a reduction peak at 350 °C, according to: CaRuO3 + 2H2 → Ru0 + CaO + 2H2O. All the Ru–CaO-containing materials (Ru/lime, Ru/CaO and Ru/Ca3Al2O6–CaO) show a reduction peak in the temperature range 339–351 °C (similar to CaRuO3) indicating that Ru0 is obtained through the reduction of a CaRuO3 phase. The TPR experiments were complemented with in situ Ru K-edge XANES (Fig. 1d). Linear combination fitting (LCF) using Ru foil, RuO2 and CaRuO3 as references allowed us to quantify
the evolution of these phases in Ru/Ca₃Al₂O₆-CaO (Fig. 1d) during in situ XANES TPR. Our XANES analysis shows that CaRuO₃ reduces to Ru⁰ between 260–400 °C. We could not detect any intermediate phases or segregation of RuO₂.

Additionally, using ex situ XRD analysis, the formation of metallic Ru particles after reduction at 500 °C in 10 vol% H₂/N₂ is evidenced by the appearance of, albeit weak, (101) reflections due to hexagonal Ru (P6₃/mmc space group) at ~44° (Fig. 1a). This Bragg reflection is observed in all of the Ru containing materials. Using Scherrer's equation, the average Ru crystallite sizes were estimated as: Ru/lime (18 nm) > Ru/CaO (10 nm) > Ru/Ca₃Al₂O₆-CaO (5 nm).

H₂ chemisorption was employed to quantify the amount of surface Ru (Table 1). Considering a stoichiometry factor of 1.0 of H/Ru, the quantity of surface Ru and its dispersion were determined as follows: 4.8 μmolRu gₑcat⁻¹ and 1.6% (Ru/lime) < 18.4 μmolRu gₑcat⁻¹ and 6.2% (Ru/CaO) < 37.4 μmolRu gₑcat⁻¹ and 12.7% (Ru/Ca₃Al₂O₆-CaO).

HR-SEM and HAADF-STEM images of the reduced materials are shown in Fig. 2. In HR-SEM (Fig. 2a), reduced Ru/Ca₃Al₂O₆-CaO exhibits particles of CaO or Ca₃Al₂O₆ with an average size of 90 ± 10 nm, which is a factor of 1.6–2.0 smaller than the size observed in Ru/CaO (140 ± 20 nm) and Ru/lime (170 ± 40 nm). Ru nanoparticles were observed by HAADF STEM in all of the materials (Fig. 2b and c) with average sizes determined as: 22.6 ± 2.6 nm (Ru/lime) > 11.2 ± 2.2 nm (Ru/CaO) > 5.3 ± 1.3 nm (Ru/Ca₃Al₂O₆-CaO).

3.3. CO₂ capture performance

The cyclic CO₂ capture performance of the bi-functional catalyst–sorbents (Ru/CaO, Ru/Ca₃Al₂O₆-CaO and the benchmarks Ru/lime and Ca–Ni-ex-Htlc) was assessed in a TGA (carbonation was performed in 20% CO₂/N₂ at 650 °C and calcination in CO₂ at 900 °C, Fig. 3a). The CO₂ uptake in the 1st cycle decreases in the following order: Ru/CaO (0.57 gCO₂/g) > Ru/Ca₃Al₂O₆-CaO (0.54 gCO₂/g) > Ru/lime (0.45 gCO₂/g) > Ca–Ni-ex-Htlc (0.11 gCO₂/g). The reference material Ca–Ni-ex-Htlc has a comparatively low CO₂ uptake, owing to the high content of Ni (45 wt%). After 10 cycles of repeated carbonation–calcination, the CO₂ uptake of Ru/CaO and Ru/lime has reduced appreciably to 0.16 gCO₂ gₑcat⁻¹ and 0.15 gCO₂ gₑcat⁻¹, corresponding to a capacity retention of 31% and 32%, respectively. On the other hand, a significantly higher cyclic stability was observed for Ru/Ca₃Al₂O₆-CaO and Ca–Ni-ex-Htlc, yielding a CO₂ uptake of 0.46 gCO₂/g and 0.09 gCO₂/g, respectively (corresponding to capacity retentions of respectively, 92% and 82% after 10 cycles). These findings indicate that the presence of a high Tammann temperature stabilizer, viz. Ca₃Al₂O₆ (Tₜ = 771 °C) or MgAl₂O₄ (Tₜ = 1065 °C) in, respectively, Ru/Ca₃Al₂O₆-CaO and Ca–Ni-ex-Htlc, improves the cyclic stability over ten cycles of the CO₂ uptake in these materials (although the CaO content in Ca–Ni-ex-Htlc is rather low, i.e. 21 wt%), in agreement with previous studies.

Temporally resolved carbonation profiles were acquired for each material to elucidate the origin of deactivation upon cyclic operation. Fig. 3b plots the CO₂ uptake of a series of materials in the 1st and 10th carbonation cycle as a function of time. The carbonation of CaO is known to occur in two regimes: i) a reaction stage that is kinetically controlled and in which CaCO₃ fills the volume available in small pores (d_pure < 100 nm) and ii) a diffusion-limited reaction stage that is controlled by the slow diffusion of CO₂ through the CaCO₃ product layer. The diffusivity of CO₂ through CaCO₃ (D_CaCO₃ = 0.003 cm² s⁻¹) is significantly smaller than its diffusion through CaO (D_CaO = 0.3 cm² s⁻¹). Here, we determine the transition between these two reaction stages as the intersection of two lines that fit linearly the CO₂ uptake with time in the two carbonation regimes. Owing to the large difference in the rate of carbonation in the two reaction regimes, a large fraction of the overall CO₂ uptake occurs in the kinetically-controlled regime, viz. 0.40 gCO₂/g, 0.35 gCO₂/g and 0.33 gCO₂/g for, respectively, Ru/lime, Ru/CaO and Ru/Ca₃Al₂O₆-CaO, in 1st cycle (contributing to 88%, 62% and 63% of the respective overall CO₂ uptake). However, after two cycles, the CO₂ uptake of Ru/CaO and Ru/lime in the kinetically-controlled reaction stage decreased significantly to 0.19 gCO₂/g and 0.21 gCO₂/g, i.e., a reduction by 45% and 48%,
respectively (these values reduced to 0.10 gCO2/g and 0.08 gCO2/g after 10 cycles). The decrease in the CO2 uptake is significantly less pronounced in Ru/Ca3Al2O6–CaO which can be attributed to a reduction in the extent of sintering due to the presence of the stabilizer Ca3Al2O6.

Changes in the porosity of the materials with cyclic operation were monitored by N2 adsorption. The pore size distribution of the freshly calcined materials and materials that have been exposed to 10 cycles of carbonation and regeneration are plotted in Fig. 3c (values given in Table S2†). In Ru/lime and Ru/CaO the pore volume in pores with a diameter <100 nm was reduced appreciably over 10 cycles of carbonation and regeneration, viz. from 0.11 cm3 g−1 to 0.01 cm3 g−1 and from 0.19 cm3 g−1 to 0.05 cm3 g−1, respectively. On the other hand, Ru/Ca3Al2O6–CaO retains to a larger extend its pore volume (0.23 cm3 g−1 after 10 cycles of carbonation and regeneration compared to an initial value of 0.26 cm3 g−1). The reduction in pore volume (dpore < 100 nm), highlighted in gray in Fig. 3c, agrees well with the trend observed for the decay of the CO2 uptake in the kinetically controlled regime (Fig. S5†). This observation is in line with the hypothesis that the CO2 uptake in the kinetically-controlled regime is linked directly to the pore volume available in pores with dpore < 100 nm.48,49

3.4. SE-SMR performance: first cycle

In the following the SE-SMR activity of the materials synthesized was assessed at 550 °C using a feed composition of CH4:H2O:N2 = 1:4:9 (total flow rate 14 ml min−1; GHSV = 8.4 L gcat−1 h−1). Fig. 4 summarizes the results of the Ru containing materials, whereas the activity of the benchmark Ca-Ni-ex-HTlc is plotted in Fig. S6a.† Fig. 4a plots the SE-SMR performance of Ru/lime, Ru/CaO and Ru/Ca3Al2O6–CaO (N2-free off-gas composition on a dry basis) in the 1st cycle. Generally, the SE-SMR reaction can be divided into three reaction stages. In the so-called pre-breakthrough stage (labelled i, Fig. 4a), high-purity H2 is produced. This stage is followed by a breakthrough stage (labelled ii) in which there is some CH4 slip. In addition, also CO2 and CO are detected in the effluent gas. In the post-breakthrough stage (labelled iii), the concentrations of CH4, CO, CO2 and H2 approach the equilibrium concentration of the conventional SMR, as the CO2 sorbent has been converted by a large extent to CaCO3. The exception from this reaction pattern is Ru/lime which shows a continuously increasing concentration of CH4, without any clear pre-breakthrough stage, indicative of a very poor SMR activity of this material. This is most likely due to the large Ru particle size and hence the low dispersion of Ru in this material (Table 1). On the other hand, Ru/CaO and Ru/Ca3Al2O6–CaO, show clearly all three reaction stages, indicative of a high catalytic activity of these two materials. For Ru/CaO, the mole fraction of CO2, CO and CH4 in the pre-breakthrough stage (t = 0–83 min for the 1st cycle) are very low (<0.03) yielding a H2 mole fraction of ≈0.97, which is close to the thermodynamic equilibrium (0.99) of the SE-SMR, and significantly higher than the thermodynamic equilibrium of the conventional SMR (0.75). This result implies that the CO2 that is produced during the simultaneous SMR and WGS reactions is immediately
captured by CaO, i.e., CaO + CO₂ → CaCO₃. In the post-breakthrough stage, the mole fraction of CO₂ in the off gases increases (0.18) while the mole fraction of H₂ decreases (0.67). The three characteristic stages of the SE-SMR are also observed for Ru/Cₐ₃₅Al₂O₆–CaO, yet the duration of the pre-breakthrough period is slightly shorter (t = 0–70 min) than for Ru/CaO. The most likely explanation for this observation is the lower content of CaO in this material due to the formation of CO₂-capture-inactive Ca₃Al₂O₆ (the CO₂ uptake of Ru/CaO and Ru/Cₐ₃₅Al₂O₆–CaO in the first cycle was 0.57 gCO₂/g and 0.54 gCO₂/g, respectively). The benchmark Ca–Ni-ex-HTlc has a significantly shorter pre-breakthrough period (t = 0–13 min) as this material contains 45 wt% Ni and only 21 wt% CaO (Fig. S6a†), hence possessing a lower CO₂ uptake capacity.

3.5. SE-SMR performance: cyclic performance

Fig. 4b and S6b† plot the SE-SMR performance of Ru/CaO, Ru/Cₐ₃₅Al₂O₆–CaO and Ca–Ni-ex-HTlc as a function of cycle number (1, 2, 5 and 10 cycles). Ru/CaO shows a decreasing H₂ purity in the pre-breakthrough stage over 10 cycles (decrease from 96 to 92 mole%) and a continuous increase of the concentration of CH₄ at the end of post-breakthrough stage (increase from 15 to 49 mole% over 10 cycles). Moreover, for Ru/CaO the time on stream when breakthrough occurs decreases with cycle number from 83 min (1st cycle) to 53 min, 33 min and 25 min in the 2nd, 5th and 10th cycles, respectively. On the other hand, a higher cyclic stability, i.e. a reduced decline in the duration of the pre-breakthrough period with cycle number, is observed for Ru/Cₐ₃₅Al₂O₆–CaO. After 10 cycles, Ru/Cₐ₃₅Al₂O₆–CaO and Ca–Ni-ex-HTlc retained, respectively, 92% and 76%, of the duration of the initial pre-breakthrough period compared to 29% for Ru/CaO.

Two reasons could lead to a deactivation of the materials with cycle number viz. catalyst deactivation or a reduction in the CO₂ uptake capacity of the sorbent (or a combination of both effects). To obtain further insight into the cause(s) of material deactivation and to explain the improved stability of Ru/Cₐ₃₅Al₂O₆–CaO, we investigate: 1) whether there exists a correlation between the SE-SMR performance and changes in
the CO₂ uptake capacity of the materials with cycle number, 2) the catalytic stability far from equilibrium conversion, 3) changes in the morphology of the materials and 4) the quantity of coke deposited.

3.5.1. Correlation between SE-SMR performance and CO₂ uptake. Fig. 4c plots the quantity of H₂ produced in the pre-breakthrough stage as a function of cycle number for the different materials studied. Generally, the bi-functional, Ru–CaO-based materials show a higher yield of H₂ than the benchmark Ca–Ni-ex-Htlc, due to their higher CaO content and hence extended pre-breakthrough period. Nonetheless, also Ru/ CaO and Ru/Ca₃Al₂O₆–CaO show a reduction in the duration of the pre-breakthrough period with cycle number. Fig. 5a plots the H₂ yield in the pre-breakthrough period against the CO₂ uptake for a given cycle number determined under SE-SMR mimicking conditions (Fig. S7†). This plot indicates that there is indeed a linear correlation between the CO₂ uptake and the duration of the pre-breakthrough period, hence, also the yield of high purity hydrogen.

3.5.2. SE-SMR performance in the kinetic regime. To probe material stability further, the SE-SMR reaction was also performed in the kinetic regime, far from equilibrium conversions (i.e. at a CH₄ conversion of 40% as opposed to 98% for equilibrium conditions). Specifically, the SE-SMR was operated at 550 °C with a high GHSV of 84.0 L g<sub>catalyst</sub>⁻¹ h⁻¹ (140 ml min⁻¹ of 10 CH₄/40 H₂O/90 N₂). Fig. 5b plots the rate of methane consumption (after 1 h TOS) normalized by surface Ru (quantified by H₂ chemisorption using a stoichiometric factor of H₂/M<sub>Ru</sub> or M<sub>Ru</sub>) = 1.0). For the different materials tested, the rate of CH₄ consumption in the post-breakthrough regime (after 1 h TOS) in the first cycle shows a linear relationship with the quantity of surface Ru, indicating that surface metallic Ru is the active sites for SMR. The normalized rate of CH₄ consumption (1 h of TOS) for the Ru–CaO-based materials is in the range 5–5.4 mol<sub>CH₄</sub> mol<sub>Ru</sub>⁻¹ h⁻¹, which is approximately 50% higher than for the Ca–Ni-ex-Htlc benchmark (3.6 mol<sub>CH₄</sub> mol<sub>Ru</sub>⁻¹ h⁻¹). The higher activity of Ru for the SMR compared to Ni is in line with previous findings. After 10 cycles, Ru/Ca₃Al₂O₆–CaO demonstrated a high catalytic stability, viz. the rate of the normalized methane consumption (4.2 mol<sub>CH₄</sub> mol<sub>Ru</sub>⁻¹ h⁻¹) exceeded substantially the values of Ru/lime (0.7 mol<sub>CH₄</sub> mol<sub>Ru</sub>⁻¹ h⁻¹) and Ru/CaO (0.8 mol<sub>CH₄</sub> mol<sub>Ru</sub>⁻¹ h⁻¹). Nevertheless, a gradual reduction of the normalized rate of methane consumption with cycle number was observed for Ru/Ca₃Al₂O₆–CaO (Fig. 5c), pointing to a deactivation of the catalyst.

3.5.3. Characterization of bifunctional Ru–CaO materials after cyclic SE-SMR reaction. Textural changes over repeated SE-SMR cycles were probed by N₂ adsorption (Table S3 and Fig. S8†). In particular, the Al-free materials show an appreciable reduction in the pore volume and surface area, viz. S<sub>BET</sub> = 5 m<sup>2</sup> g<sub>catalyst</sub>⁻¹ and V<sub>pore</sub> = 0.06 cm<sup>3</sup> g<sub>catalyst</sub>⁻¹ for Ru/lime and S<sub>BET</sub> = 6 m<sup>2</sup> g<sub>catalyst</sub>⁻¹ and V<sub>pore</sub> = 0.07 cm<sup>3</sup> g<sub>catalyst</sub>⁻¹ for Ru/CaO. On the other hand, the textural characteristics of Ru/Ca₃Al₂O₆–CaO are largely maintained (S<sub>BET</sub> = 18 m<sup>2</sup> g<sub>catalyst</sub>⁻¹ and V<sub>pore</sub> = 0.21 cm<sup>3</sup> g<sub>catalyst</sub>⁻¹ after 10 cycles of SE-SMR compared to the initial values of S<sub>BET</sub> = 23 m<sup>2</sup> g<sub>catalyst</sub>⁻¹ and V<sub>pore</sub> = 0.26 cm<sup>3</sup> g<sub>catalyst</sub>⁻¹). The substantial changes in the textural properties of Ru/lime and Ru/CaO with repeated SE-SMR/regeneration cycles are also visualized by HR-SEM (Fig. 6a).

Turning to the growth of the Ru nanoparticles, analysis of HAADF STEM images (freshly reduced, Fig. 2, and spent materials, Fig. 6b) reveals an increase in the size of the Ru particle size from 5.3 ± 1.3 nm to 8.4 ± 2.0 nm for Ru/Ca₃Al₂O₆–CaO after 10 cycles (Fig. 6c). However, this particle size is still 2.7 and 4.0 times smaller than that of spent Ru/CaO (22.5 ± 4.2 nm) and Ru/lime (33.5 ± 3.6 nm), respectively. The trend in the Ru particle size as determined by HAADF STEM is in good agreement with the trend in surface Ru as quantified by H₂ chemisorption (Table S3†): Ru/Ca₃Al₂O₆–CaO (31.5 μmol<sub>Ru</sub> g<sub>catalyst</sub>⁻¹) > Ru/CaO (7.2 μmol<sub>Ru</sub> g<sub>catalyst</sub>⁻¹) > Ru/lime (2.1 μmol<sub>Ru</sub> g<sub>catalyst</sub>⁻¹). These measurements provide strong evidence that the decrease in the rate of methane consumption is due to the sintering of Ru particles.
3.5.4. Extent of coke formation. To probe the extent of coke formation, materials that have undergone 10 SE-SMR/regeneration cycles were collected (after the SE-SMR step) and characterized by TPO (Fig. 7a). The weight increase of Ca–Ni-ex-Htlc in the temperature range 300–500 °C is due to the oxidation of Ni to NiO. On the other hand, the weight increase of Ru-containing materials in the temperature range 100–600 °C was negligible. The weight loss due to the oxidation of carbonaceous species occurs in the temperature ranges of 650–750 °C and 610–850 °C for Ru–CaO-containing materials and Ca–Ni-ex-Htlc, respectively. The quantity of carbon deposited increased in the following order: Ru/lime (1.1 wt%) < Ru/CaO (3.4 wt%) < Ru/Ca3Al2O6–CaO (5.4 wt%) < Ca–Ni-ex-Htlc (56.2 wt%). The small amount of carbon deposited on Ru/lime is probably due to the rather poor SMR activity of this material. Fig. 7b plots the carbon yield, i.e. the accumulated amount of carbon per mole of reacted CH4 over 10 SE-SMR/regeneration cycles. Ru/Ca3Al2O6–CaO showed a significantly lower carbon yield (41 μmolC molCH4⁻¹) compared to Ru/CaO (165 μmolC molCH4⁻¹), Ru/lime (177 μmolC molCH4⁻¹) and Ca–Ni-ex-Htlc (184 μmolC molCH4⁻¹). Furthermore, the rate of carbon formation normalized by surface Ni or Ru (as determined by chemisorption, Fig. 7b) shows the following trends: Ru/Ca3Al2O6–CaO (3.6 mmolC molRu⁻¹ s⁻¹) < Ru/CaO (4.4 mmolC molRu⁻¹ s⁻¹) < Ru/lime (5.6 mmolC molRu⁻¹ s⁻¹) < Ca–Ni-ex-Htlc (8.2 mmolC molNi⁻¹ s⁻¹). Carbon formation is favored at step and edge sites of metallic Ni and Ru, which are dominant in large particles (>5 nm). Therefore, the higher amount of coke deposited on Ru/lime and Ca–Ni-ex-Htlc, when compared to Ru/CaO and Ru/Ca3Al2O6–CaO, is due to the larger Ru and Ni particles in these systems. Hence, bi-functional, Ru-based materials allow a significant reduction of the loading of the active catalyst, and hence a higher fraction of CaO, but also reduce the extent of carbon formation. However, the high costs of Ru are a disadvantage.

4. Conclusions

We have developed a highly active and stable, Ru/Ca3Al2O6–CaO bi-functional SE-SMR material. XRD and XAS measurements of the as-synthesized (calcined) materials showed the formation of mixed oxides between CaO and the stabilizer, viz. Ca3Al2O6 and the catalyst, i.e. CaRuO3. In situ XAS measurements complemented by H2-TPR and XRD revealed the formation of metallic Ru upon reduction. Owing to the high activity of Ru for the SE-SMR, the fraction of CO2-capture-active CaO could be increased significantly when compared to the benchmark Ca–Ni-ex-Htlc, extending the pre-breakthrough duration and the yield of high-purity H2. The presence of Ca3Al2O6 in the material stabilized effectively the...
material against sintering. Furthermore, Ru/\(\text{Ca}_3\text{Al}_2\text{O}_6\)–CaO showed very little coke formation when compared to Ca–Ni-ex-Htlc. Nonetheless, the high costs of Ru are a disadvantage and further work shall concentrate on reducing further the quantity of Ru in the material while maintaining its high activity.

**Conflicts of interest**

There are no conflicts to declare.

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