Methane partial oxidation over a LaCr$_{0.85}$Ru$_{0.15}$O$_3$ catalyst: Characterization, activity tests and kinetic modeling

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A B S T R A C T
A new LaCr$_{0.85}$Ru$_{0.15}$O$_3$ perovskite-type catalyst for CH$_4$ partial oxidation with a high activity and selectivity for syngas with good thermal stability and resistance against coking has been developed. In this paper, the catalyst preparation method, catalyst characterization, results of catalytic tests in a micro-reactor and kinetic modeling are discussed. A partial incorporation of Ru in the perovskite support has been demonstrated which can be responsible for the reported high activity and stability for this catalyst. Reactivity tests have been carried out at both low and high GHSV regimes ($\approx 1\text{–}2 \times 10^7 \text{ h}^{-1}$); for the latter case the CH$_4$–O$_2$ partial oxidation reaction system has been studied at incomplete methane (7–18%) and O$_2$ (20–65%) conversion, as rarely reported in the literature. The variation of temperature (650–850 °C) and feed gas composition (in terms of CH$_4$, CO, CO$_2$, H$_2$ and H$_2$O inlet partial pressure) allowed to study the reaction system over a wide range of experimental conditions gaining insight in the reaction mechanism. A kinetic model is proposed where CH$_4$ partial oxidation, H$_2$ and CO oxidation and water–gas shift are used to describe the involved lumped reaction network. External diffusion resistances have been found to be negligible whereas internal diffusion resistances have been accounted for by means of a single particle model able to describe the concentration profiles inside the catalyst pellet. Pre-exponential factors and activation energy values for all reactions have been estimated by means of a least square fitting of the experimental data. It is found that CH$_4$ partial oxidation dominates the first region of the catalyst bed while H$_2$ and CO oxidation become important in the remaining part of the bed.

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1. Introduction

Efficient synthesis gas production from natural gas is becoming an increasingly important step for different chemical processes, and in particular for converting natural gas to liquid fuels (GTL). Steam reforming is currently the most important industrial and exploited process for the production of syngas from hydrocarbons. Nevertheless, steam reforming is a very energy-intensive process, in which overheated steam in a H$_2$O/CH$_4$ molar ratio slightly higher than stoichiometric value is used to avoid carbon deposition. In this context, new processes for syngas production with higher energy efficiencies are being evaluated.

Partial oxidation processes are attractive alternatives because they avoid the need of large amounts of superheated steam and they need smaller reactors because of the faster oxidation reactions [1]. Another advantage of direct partial oxidation is an outlet H$_2$/CO ratio of 2:1 which allows a straightforward syngas utilization for methanol or Fischer–Tropsch synthesis. Partial oxidation of methane (POM) to synthesis gas is represented by the lumped Eq. (1).

$$\text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \quad (1)$$

The active catalysts for partial oxidation are very similar to the supported metals used in steam reforming. The high reaction temperature required for partial oxidation reactions requires the use of catalysts with extreme thermal stability; this requirement puts strenuous demands on the catalyst materials in their agglomeration and vaporization resistances and structural/morphological stabilities. Additionally, resistance against carbon deposition is also a key challenge for partial oxidation catalysts. This is even more important when the partial oxidation is carried out in a membrane reactor.
with oxygen addition through membranes as the temperatures are different than in conventional reactors and the local oxygen concentration is much lower. At present, the state-of-the-art partial oxidation catalysts consist of metals from Group VIII (Ni, Co, Fe, Pd, Pt, Ru and Rh) supported onto various high surface area oxide substrates such as modified α-Al2O3, stabilized ZrO2 or mixed metal oxides [2–9]. It has been reported that catalyst deactivation by carbon is influenced by the catalyst size of the active metal, the larger metal clusters showing a much stronger interaction with carbon compared with the smaller, well-dispersed metal particles [10,11]. Thus control of the size of the active metal surfaces is important in the development of catalysts with improved catalytic activity and stability. Mixed metal oxides have become increasingly popular as catalysts for partial oxidations because of the possibility to substitute different metals into their structure while maintaining their activity [12–14]. Atomic dispersion of the active metals throughout the structure may avoid the formation of larger metal clusters at the surface that are favorable sites for carbon deposition. Perovskite type oxides (ABO3) are considered interesting alternative catalysts for partial oxidations since these oxides are able to form, under reaction conditions, well dispersed metallic particles, which increase hydrogen formation and prevent deactivation by coke. Lanthanum chromite perovskite (LaCrO3) is of considerable interest because of its stable structure, where inserted active metals lead to atomic clusters at the surface with high activity and stability under reforming conditions. By anchoring the catalytically active element into this stable crystal lattice, an improved thermal stability and carbon tolerance can be achieved compared with catalysts consisting of finely dispersed metal particles on the surface of an oxide. In this work, Ru has been chosen as active metal in the B-site taking into account its probeed activity and resistance to coke formation in reforming reactions [15].

Two mechanisms have been proposed in the literature to explain the formation of syngas by methane partial oxidation: (i) the indirect reforming reaction mechanism [16] and (ii) the direct partial oxidation mechanism [17,18]. The direct mechanism postulates the direct formation of H2 and CO as primary products by recombination of CH4 and O species at the surface of the catalysts, eventually further oxidized into CO2 and H2O, depending on process conditions (contact time, O/C ratios, etc.). The main evidence in favor of a direct path is the observation of syngas at extremely short contact times, in the presence of unreacted oxygen. The indirect pathway postulates that methane is first totally oxidized to CO2 and H2O (in a strongly exothermic reaction) and after that reformed to produce CO and H2 (by strongly endothermic reactions). One major proof of the existence of such an exothermic–endothermic sequence has been the observation of sharp hot spots at the entrance of the reactor. Irrespective of the dominating mechanism prevailing during catalytic partial oxidations, the contribution of different reactions is typically taken into account (11 reactions according to [19]), in which CO2 and steam are always found as additional reactive species in the product gas, and carbon formation may also be included as deactivating factor. It is widely recognized that a set of only 3 linearly independent reactions (Eqs. (2–4)) can reasonably describe the reaction kinetics of the partial oxidation system, viz.

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]  
\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \]  
\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \] 

Also dry reforming (Eq. (5)) is often considered [20] although this is also implicitly included in the previous 3-reactions system as the sum of steam reforming and reverse water-gas shift

\[ \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \]  

The combined kinetics of these three or four reactions is often used to describe the methane partial oxidation reaction rate in experimental [16] and modeling studies [21,22], and to the best of the authors’ knowledge a detailed analysis on the reaction kinetics over a wide range of residence times is lacking in the literature.

The study of the partial oxidation system has often been reported in literature for low-medium gas-hourly space velocity (GHSV) regimes, showing experimental data close to the equilibrium composition. The partial oxidation mechanism was found to primarily depend on the applied reaction conditions. At space times sufficiently long to obtain the equilibrium methane conversion and synthesis gas selectivity, the indirect CPO reaction mechanism seems to prevail on the catalysts [16,23]. At very short space times, however, Pt- and Rh-catalysts were found to yield conversion strongly deviating from the equilibrium conversion with a high selectivity toward syngas products [24,25], evidencing the direct
formation of H₂ and CO as primary products of the catalytic partial oxidation of CH₄. However, an investigation as a function of different feed gas compositions (CH₄, O₂, CO₂, CO, H₂, H₂O) has not been carried out in these studies; as it will be discussed in this paper this type of investigation can provide additional information on the understanding of the parallel and series reactions that play a role next to CH₄ (partial) oxidation at high GHSV.

This work aims to study the methane partial oxidation reaction system over a Ru-based perovskite catalyst. The newly synthesized catalyst has been characterized by BET, XPS, X-ray diffraction and H₂-TPR (Temperature Programmed Reduction) analysis. Low GHSV conditions have been used to test LaCr₀.₈₅Ru₀.₁₅O₃ stability and selectivity, and the analysis of both crystalline structure and morphology of the used catalyst is further reported. High GHSV have also been adopted in order to obtain non-equilibrium conversions for the methane partial oxidation reaction system at different experimental conditions such as temperature and species concentrations in the feed. The obtained kinetic results have been used to develop a simple “lumped” kinetics model for the CH₄→O₂ reaction system. The medium-high temperature range covered in this paper also aims to supply additional data on reaction kinetics in a scarcely investigated range, especially because of mass transfer limitations often encountered [25]. The effect of intra- and inter-particle diffusion resistances has been evaluated in order to extract the intrinsic kinetics of the involved reactions in terms of activation energies and pre-exponential factors.

2. Experimental procedure

2.1. Catalyst preparation

LaCr₀.₈₅Ru₀.₁₅O₃ perovskite was synthesized by a modified citrate sol-gel method [2]. 1 M aqueous solutions of La(NO₃)₃·6H₂O (99.9% Alfa Aesar), Cr(NO₃)₃·6H₂O (99.9% Alfa Aesar) and RuCl₃ (40.49% Ru, Johnson Matthey) were added to a solution of citric acid (Alfa Aesar) and ethylene glycol (Riedel-de Haën) in adequate amounts: citric acid/(A-cation + B-cation) = 2.5 mol, and ethylene glycol/citric acid = 1 mol. The aqueous mixture was stirred and slowly heated to 70 °C for 2 h until a resin was formed. The resultant resin, which contains the metal cations inside a polymeric network, was charred at 300 °C for 2 h with a heating rate of 1 °C min⁻¹. After that, the resin was milled to obtain a fine powder and calcined under air at 750 °C for 4 h with a heating rate of 2 °C min⁻¹.

2.2. Physico-chemical characterization

The BET surface area of the LaCr₀.₈₅Ru₀.₁₅O₃ perovskite was measured by adsorption/desorption of nitrogen at −196 °C, taking a value of 0.162 nm² for the cross-section of a N₂ molecule adsorbed at this temperature. The measurement was performed with a Micromeritics ASAP 2100 apparatus on samples previously degassed at 200 °C for 20 h. The experiments were performed at liquid nitrogen temperature (−196 °C) using the quasi-Gemini method to minimize errors in the measurement of low area samples. XRD patterns of perovskite were recorded using a Seifert 3000P vertical diffractometer and nickel-filtered Cu Kα radiation (λ = 0.1538 nm) under constant instrumental parameters. Bragg angles between 5° and 90° were scanned; a rate of 5 s per step (step size: 0.04°) was used during a continuous scan in the above-mentioned range. The mean crystalline particle size was estimated from X-ray line width broadening using the Scherrer equation. Width (t) was taken through the full width at half maximum intensity of the most intense and least overlapped peaks. XPS measurements were registered using an Escalab 200R spectrometer equipped with a hemispherical electron analyzer and an Al Kα (hv = 1486.6 eV, 1 eV = 1.6302 × 10⁻¹⁹ J) 120 W X-ray source. The area of the peaks was estimated by calculating the integral of each peak after smoothing and subtraction of an S-shaped background and fitting of the experimental curve to a mixture of Gaussian and Lorentzian lines of variable proportions. All binding energies (BE) were referenced to the C 1s signal at 284.6 eV from carbon contamination of the samples to correct the charging effects. Quantification of the atomic fractions on the sample surface was obtained by integration of the peaks with appropriate corrections for sensitivity factors. Hydrogen temperature-programmed reductions (H₂-TPR) of the perovskite were conducted using a PID Eng & Tech instrument in a U-shaped quartz reactor. Prior to the reduction experiments, the sample (15 mg) was flushed with a helium stream at 110 °C for 15 min and then cooled down to room temperature. TPR profiles were obtained by heating the sample under a 10% H₂/Ar flow (50 mL/min⁻¹) from 30 to 700 °C (1 h at 700 °C) at a linearly programmed rate of 10 °C min⁻¹. The fraction of carbonaceous residues in the catalysts after activity tests was determined by temperature programmed oxidation thermo-gravimetric analysis (TGA/SDTA 851e Mettler Toledo). Analyses were carried out by raising the sample temperature from 298 to 1123 K at a rate of 5 K min⁻¹ in a 20% O₂/N₂ flux.

2.3. Activity tests

The stability and selectivity of the LaCr₀.₈₅Ru₀.₁₅O₃ catalyst formulation was tested for methane oxidative reforming at low GHSV. The catalytic bed was made of 100 mg of catalyst grounded to 0.200–0.425 mm diluted with carborundum (dp = 0.5 mm, SiC/catalyst = 3.0 volume) to avoid preferential gas flow paths and hot spots in the catalytic bed. Catalytic bed was placed in a fixed-bed continuous flow stainless steel reactor (8 mm i.d.) with a coaxially centered thermocouple in contact with the catalytic bed. The auto thermal reforming of methane (CH₄ + H₂O + O₂: He to 1: 1: 0.75: 2.5) was performed at atmospheric pressure and at 850 °C, maintaining the reaction for 8 h at this temperature. The flow rates of gases were adjusted by mass flow rate controllers with a total gas flow rate of 200 N mL min⁻¹ (GHSV = 10,660 h⁻¹). N₂ (2 mL min⁻¹) was also fed to the feed as internal standard. The GHSV is defined in this work as (total volumetric flow entering the reactor, STP)/[catalyst volume]. The products were analyzed periodically by an on-line gas chromatograph (HP 5890 Series II) equipped with a TC detector and programmed to operate under high-sensitivity conditions. A 4A molecular sieve column is used for H₂, O₂, N₂, CO and CH₄ separation and a Porapack N (80/100) for separated CO₂ and H₂O detection. Activity data were reported as methane conversion (X(CH₄)) and yield (Y) to H₂, CO and CO₂, which are defined as follows:

\[
\begin{align*}
X(CH₄)(\%) &= \frac{n(CH₄)_{out} - n(CH₄)_{in}}{n(CH₄)_{in}} \times 100 \\
Y(H₂)(\%) &= \frac{n(CH₄) \times (n(H₂)_{out} \times n(H₂O)_{out})}{n(CH₄)_{in} \times n(H₂O)_{in} \times n(H₂O)_{out}} \times 100 \\
Y(CO)(\%) &= \frac{n(CH₄) \times n(CO)_{out}}{n(CH₄)_{in} \times n(CO)_{out} + n(CO₂)_{out} + n(CO)_{out}} \times 100 \\
Y(CO₂)(\%) &= \frac{n(CH₄) \times n(CO₂)_{out}}{n(CH₄)_{in} \times n(CO₂)_{out} + n(CO₂)_{out} + n(CO)_{out}} \times 100 
\end{align*}
\]

High GHSV catalytic experiments were carried out at atmospheric pressure in a U-shaped quartz reactor (1 cm i.d.) placed in an electric furnace. A scheme of the experimental setup can be found in Fig. S1 (supplementary information). The catalytic bed consisted of 30 mg of catalyst (100 < dp < 150 μm) mixed with 3 g of inert quartz particles (200 < dp < 1000 μm). The gas entering the reactor is fed from the top of the catalytic bed, which in turn is housed
in a plug of quartz wool blocked by an underneath restriction of reactor walls. This configuration avoids entrainment of catalytic particles in the high gas velocity regime, which is well above the terminal velocity of the catalyst particles. Before the catalytic tests, the samples were reduced under a 30% H₂/N₂ flow using conditions derived from TPR profiles (100 NmL min⁻¹, T = 800 °C for 2 h). The temperature was measured by a thermocouple located in the radial center of the reactor, about 2 cm downstream of the catalytic bed. An additional thermocouple has been located just below the bed, measuring the gas temperature close to the outlet of the packed bed reactor. The outlet gas has been analyzed by a Varian CP-4900 micro-GC equipped with two Molecular Sieve 5 Å PLOT and one PPQ (PorapLOT-Q) columns to measure the concentration of H₂, CH₄, CO, CO₂, O₂, and N₂. Calibrators (Bios Definers) have been used for accurate measurement of the volumetric flow rates in the range 5–30,000 mL min⁻¹. The error in the C balance has been found to be in the order of only 1%.

Supplementary Fig. S1 related to this article can be found in the online version, at http://dx.doi.org/10.1016/j.apcata.2014.08.040.

The catalyst was tested with an overall feed flow rate of about 5.4 NmL min⁻¹ with a molar composition ratio of CH₄/O₂/N₂ equal to 1:0.34:6.3, to investigate the effect of temperature (in the range 650–850 °C) on CH₄ conversion (tests 1–2). A GHSV of 1.7 × 10⁻³ h⁻¹ (measured at STP conditions) was used in these experiments. In further tests, a constant temperature has been retained (760 °C) and the effect of inlet species composition has been investigated, at constant inlet N₂ flow (tests 3–8). In particular, the inlet flow rates of the gas species were varied within the following ranges: CH₄ 700–1220 mL min⁻¹, O₂ 120–280 mL min⁻¹, H₂ 0–120 mL min⁻¹, CO 0–75 mL min⁻¹, H₂O 0–300 mL min⁻¹. The test number reflects the sequence at which the experiments have been carried out in the laboratory, from 1 (first test) to 9 (last test).

3. Experimental results

3.1. Catalyst characterization

Specific surface areas of the calcined perovskite shows a low value in line with the low surface areas typically observed for perovskite systems. Nevertheless, the partial substitution of chromium atoms by Ru provokes an increase in the surface area (6.7 m² g⁻¹) developed by the pure LaCrO₃ perovskite (5.2 m² g⁻¹) indicative of changes in the particle size of perovskites, in the aggregation of particles or in the segregation of species with low size and high external surface area.

Fig. 1 shows the X-ray diffraction patterns of the calcined perovskite catalyst. The XRD pattern of the pure as-prepared LaCrO₃ exhibits strong reflections that correspond to a well-defined orthorhombic perovskite structure with a high degree of crystallinity and homogeneity (JCPD-24-1016). The XRD pattern of LaCr₀.₈₅Ru₀.₁₅O₃ exhibits a diffraction pattern similar to that detected for pure LaCrO₃. The presence of Ru produces a shift of the perovskite diffraction lines to higher Bragg angles. This phenomenon is indicative of an expansion in the perovskite LaCrO₃ lattice due to the substitution of the Cr by Ru of higher atomic radius. Moreover, weak diffraction lines assigned to La₂CrO₆ crystalline phase, LaRuO₃ structure and RuO₂ segregated species can be observed. The crystalline sizes of pure and Ru-substituted chromites were also evaluated using the Scherrer equation. It is observed that the crystalline size increases in the LaCr₀.₈₅Ru₀.₁₅O₃ sample (35.8 nm) with respect to pure LaCrO₃ perovskite (28.7 nm). This fact could be associated to the structural modifications of lanthanum chromite originated by the insertion of Ru ions into the chromite structure. The size of the crystalline domains calculated by XRD and BET surface area values of LaCr₀.₈₅Ru₀.₁₅O₃ and pure LaCrO₃ showed similar trend, LaCr₀.₈₅Ru₀.₁₅O₃ > LaCrO₃. This trend does not agree with the common correlation indicating that surface and the particle size of perovskites follow opposite trends since the surface is determined by the geometrical external area of particles without internal porosity. Therefore, the observed absence of the correlation between surface and particle size could be derived from a different grade of aggregation of the individual crystalline particles of perovskite (LC–Ru > LC) [26] or by the segregation of species with low particle size to be detected by XRD and high surface area (La₂O₃, CoO₃ or RuO₂ not detected by XRD).

Fig. S2 (supplementary information) shows the H₂ consumption profiles registered during temperature-programmed reduction experiments over the prepared LaCr₀.₈₅Ru₀.₁₅O₃ sample. Since LaCrO₃ perovskite is known to be stable under reductive atmospheres [27], the little hydrogen consumption detected for pure lanthanum chromite (LC) sample, at ca. 352 °C (0.048 mol H₂/mol perovskite), is attributed to the reduction of surface OH groups and adsorbed oxygen [28]. The LaCr₀.₈₅Ru₀.₁₅O₃ sample showed a complex TPR profile associated with the reduction of different species. Reduction peaks observed for these samples at ca. 352 °C could be related to the reduction of surface —OH and —O species. In the case of Ru-loaded lanthanum chromite (LC–Ru), the two intense peaks at 177 and 210 °C are attributed to the reduction of segregated Ru oxides species with different interaction with the bulk lanthanum chromite perovskite [29]. The lower temperature TPR peak has been assigned to the reduction of well-dispersed RuO₂ species, and the high-temperature peak is attributed to the reduction of RuO₂ particles. Quantitative analysis of the H₂ consumption observed for LaCr₀.₈₅Ru₀.₁₅O₃ perovskite

![Fig. 1. XRD patterns of fresh (A) and used (B) ATIR catalysts (+: LaCrO₃ orthorhombic, O: LaRuO₃ orthorhombic, *: RuO₂ tetragonal, S: SiC).](image-url)
Table 1
XPS La 3d, Cr 2p and Ru 3p binding energies (eV) and surface atomic ratios of the lanthanum chromites (LaCrO₃ (reference), LaCr₀.₈₅Ru₀.₁₅O₃).

<table>
<thead>
<tr>
<th>Binding energy (eV)</th>
<th>Surface atomic ratio (atomic %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>La</td>
</tr>
<tr>
<td>LaCrO₃ (reference)</td>
<td></td>
</tr>
<tr>
<td>La 3d₅/₂</td>
<td>834.1</td>
</tr>
<tr>
<td>Cr 2p₃/₂</td>
<td>575.8 (38)</td>
</tr>
<tr>
<td>Ru 3p₃/₂</td>
<td>0.403 (0.5)</td>
</tr>
<tr>
<td>LaCr₀.₈₅Ru₀.₁₅O₃</td>
<td></td>
</tr>
<tr>
<td>La 3d₅/₂</td>
<td>834.3</td>
</tr>
<tr>
<td>Cr 2p₃/₂</td>
<td>575.9 (59)</td>
</tr>
<tr>
<td>Ru 3p₃/₂</td>
<td>463.7</td>
</tr>
<tr>
<td></td>
<td>0.53 (0.5)</td>
</tr>
</tbody>
</table>

(0.275 mol H₂/mol perovskite) indicates the reduction of segregated RuO₂ species that corresponds to around 45% of the total Ru loaded in the perovskite structure.

Supplementary Fig. S2 related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2014.08.040.

Photoelectron spectroscopy analyses were performed in order to determine the chemical state of the elements and their surface proportions on the catalysts. The binding energies of La 3d, Cr 2p and Ru 3p core levels and the surface atomic ratios obtained by this technique are displayed in Table 1. The La 3d core level exhibits a main component of the La 3d₅/₂ core level at binding energies of 834.0–834.3 eV attributed to the presence of La³⁺ in perovskite-type environment. The Cr 2p level could be resolved, after curve fitting procedures, into two components with binding energies of ca. 576 and 579 eV. These two contributions can be related to Cr³⁺ and Cr⁵⁺/Cr⁶⁺, respectively [30]. In relation to the chemical state of Ru species, the Ru 3p₃/₂ core level of perovskites show a main component at 463.7–464.4 eV characteristic of the presence of Ru⁴⁺ species on the surface of all samples [31]. These results are in accordance with the RuO₂ compounds detected by TPR analysis (Fig. S2). The surface concentration of La, Cr and Ru calculated from XPS intensities is presented in Table 1. It is observed that the Cr/La ratio decreases in the LaCr₀.₈₅Ru₀.₁₅O₃ perovskite with respect to the bare LaCrO₃ indicating a loss of Cr exposition on the surface induced by the presence of the Ru. The Ru surface exposure in LaCr₀.₈₅Ru₀.₁₅O₃ sample is higher than the expected nominal value in accordance to the presence of segregated RuO₂ species detected by TPR.

Fig. 2. TEM micrographs of the used LaCr₀.₈₅Ru₀.₁₅O₃ catalyst.
3.2. Activity test in the oxidative reforming of methane

The conversion of methane and the product distribution for the oxidative reforming of methane achieved at steady state (ca. 12 h on stream) were quantified over the LaCr0.85Ru0.15O3 catalyst and the reference LaCrO3. The unsubstituted LaCrO3 exhibits low reforming activity and produces mainly CO2 (38% yield) as the product of the total oxidation at a CH4 conversion of 36%. With this catalyst, the production of H2 and CO is quite low (1.4 and 4.7% yield, respectively). LC–Ru shows a very high yield to H2 and CO production (46 and 65% respectively) and stable CH4 conversion close to 100% for the 12 h duration of the test.

The crystalline structure of the catalysts after the activity tests was analyzed by XRD and the diffraction patterns are displayed in Fig. 1. The crystalline structure of the catalyst was maintained after the reactivity tests showing the reflections associated to the orthorhombic LaCrO3 structure with no evolution of segregated ruthenium oxides species. The average particle size of the orthorhombic LaCrO3 phase in the used catalysts by application of the Scherrer equation were similar (LaCr0.85Ru0.15O3 = 36 nm, LaCrO3 = 28 nm) to that calculated for the fresh catalysts, indicating this fact the absence of sintering processes under reaction conditions. Reflections attributed to graphitic carbon were not detected in any case, in line with the very limited carbon formation during oxidative reforming of methane over the LaCr0.85Ru0.15O3 catalyst as observed by TGA analyses performed on used samples. The TGA analysis of used LaCr0.85Ru0.15O3 catalyst (not shown here) did not exhibit any significant mass loss associated to the presence of carbonaceous deposits on the catalyst.

The morphology of the used catalysts was also studied by TEM. As can be observed from Fig. 2 all the samples present irregular aggregates constituted by nanometric particles. According to EDX analysis, after the activity tests, the surface concentration of the LaCr0.85Ru0.15O3 catalyst is quite homogeneous and consistent with values expected for the corresponding lanthanum chromite composition (Cr/La = 0.79 and Ru/La = 0.09). The images taken from the LaCr0.85Ru0.15O3 used catalyst display particles with spherical shape without detecting the presence of neither segregated phases nor graphitic structures.

3.3. Kinetic study of the partial oxidation of methane at high GHSV

Experimental tests reported in this section have been carried out using the experimental rig described in Section 2.3. A virtually linear increase in the CH4 and O2 conversion is reported for increased temperatures (tests 1–2 at constant inlet composition), as shown in Fig. 3A. The CO selectivity is expressed as

\[
S_{\text{CO}}(\%) = \frac{n_{\text{CO}}}{n_{\text{CO}} + n_{\text{O2}}} \times 100
\]

and is shown in Fig. 3B together with the obtained H2/O2 ratio as a function of the temperature. The CO selectivity increases for higher operating temperatures, as also reported previously by other authors at high GHSV and incomplete O2 conversion [23,32]. The observed CO selectivity (20–50%) is a preliminary indication that CO2 formation reactions have to be accounted for in the proposed reaction scheme. Moreover, the H2/O2 ratio decreases from 3 to 1.5 over the investigated temperature range, evidencing that the net H2 production rate is lower than the net CO production rate at higher temperatures. A significant contribution from a hydrogen consuming reaction such as H2 oxidation can be considered to explain this behavior, as reported by other authors [24].

Tests 3–8 were started (and ended) with a base case – at reference conditions reported in Section 2.3, T = 760 °C – to investigate whether deactivation phenomena prevailed during or between catalytic runs; the comparison is shown in Fig. S3 (supplementary information) in terms of CH4 conversion of the base-case for each different test, where a good catalyst stability over time was found. Supplementary Fig. S3 related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2014.08.040.

The effect on CH4 conversion for different CH4, O2, CO2 and H2O feed compositions is shown in Fig. 4A–D respectively. It can be noticed that the CH4 conversion increases by increasing both CH4 and O2 reactant partial pressures while keeping the concentrations of the other reactants constant, whereas a progressive increase of CO2 and H2O feeding partial pressures do not show any significant effect on.

A small decrease in CH4 conversion when H2 is co-fed with CH4, O2 and N2 has been observed (Fig. 5A). This can most likely be attributed to the increased O2 conversion because of H2 oxidation, resulting in less O2 available for CH4 oxidation. On the other side, an increase in O2 conversion is not observed when CO is co-fed (Fig. 5B); the increased outlet CO2 (about 15 mL min⁻¹ of additional CO2 produced when the CO inlet flow rate is increased from 0 to 75 mL min⁻¹), can more likely be ascribed to the WGS reaction which apparently also plays a role in the reaction mechanism.

4. Mechanism and modeling

4.1. Selection of the kinetic mechanism

Different mechanisms were tested to describe the experimental data on catalytic auto thermal reforming. Separate experiments
(not shown here) have been carried out at the same GHSV and temperature range adopted for the CH₄ partial oxidation tests, feeding 700 mL min⁻¹ of CH₄ and a range of 150–450 mL min⁻¹ of steam. It has been confirmed that steam reforming takes place – about 50 mL min⁻¹ of CH₄ being consumed at these conditions.

For this reason, it would seem a good approach to consider both steam reforming and methane total oxidation in the mechanism, as well as WGS, CO, and H₂ oxidation. However, despite the evidences of reforming activity, the best mechanism describing the experimental results is via the partial oxidation of methane as a correct pathway to produce hydrogen instead of steam reforming as it will be explained below.

The main steps identified to describe the reaction system for the LaCe₀.₈₅Ru₀.₁₅O₃ catalyst are, respectively:

1. CH₄ partial oxidation where H₂ and CO are produced
   
   \[ CH₄ + \frac{1}{2} O₂ → CO + 2H₂ \]

2. Produced H₂ can undergo oxidation where more steam is produced
   
   \[ H₂ + \frac{1}{2} O₂ → H₂O \]

3. Besides, carbon monoxide can also react with O₂ (oxidation) to form CO₂
   
   \[ CO + \frac{1}{2} O₂ → CO₂ \]

4. Produced CO can competitively react with H₂O (WGS)
   
   \[ CO + H₂O ⇌ CO₂ + H₂ \]

The reasons why we chose to include partial oxidation and exclude methane steam reforming are the following:

- A first fitting of steam reforming and water gas shift kinetic parameters was performed using the experimental data with CH₄ and H₂O feeding. Afterwards, the obtained parameters were used to describe the experiments with oxygen, adding the oxidation reactions and fitting their kinetic parameters separately. It was found that the previously obtained kinetics of steam reforming reaction were incompatible with the experimental data of partial oxidation, and no good agreement between calculations and experiments could be achieved. In particular, the temperature dependency governing the production of hydrogen calculated by the reforming tests was too high for the partial oxidation tests.

The experimental data on partial oxidation proved that the CH₄ conversion rate does not depend on the steam partial pressure. A description of the partial oxidation tests including steam reforming is possible only by assuming a particular form of the SR reaction rate expression that takes this into account. Fitting the kinetic parameters for steam reforming and methane total oxidation on the partial oxidation data resulted in a good agreement with the experimental data. Nevertheless, fitting the same experimental data with the partial oxidation mechanism presented above ended up in an even better agreement, and with a lower number of parameters.
The experimental work presented in this paper seems to confute the general idea that auto thermal reforming is just about carrying out a fast oxidation of methane, followed by slower reforming with the produced steam. This is proved by the fact that both oxygen and hydrogen are present in the products. The model optimizations on data sets with and without oxygen also suggest that there seems to be a change in the pathway to form hydrogen when oxygen is added to the system.

One possible explanation of this could be related to the different oxidation state of the catalyst, particularly of Ru, when oxygen is present in the reaction atmosphere. A different conformation of the active site may deeply change the kinetics rates, as remarked by Omata et al. [33] for the K–Ni based AT catalyst, or even the reaction pathway. Considering the experimental data on auto thermal reforming presented in the previous section, in all cases the oxygen conversion was not very high, which means that the catalyst composition can be assumed to be uniform and constant.

4.2. Mathematical model

The experimental results have been fitted by making use of an isothermal PFR model, consisting of component mass balances and the total mass balance:

\[ \frac{d c_i^0}{dz} = \rho_i \]  

(6)

\[ \frac{dc_i}{dz} = r_i \quad (i = 1, 2 \ldots n_c) \]

(7)

\[ \frac{dc_i}{dz} = \frac{\sum_{i=1}^{n_c} r_i}{D_i} \]

(8)

A total mass balance in the form of Eq. (7) was added, in order to take into account the change in velocity due to the occurrence of non-equimolar reactions.

Gas dispersion can be neglected because of the very high gas flow rates in the reactor (the Pelet number was found to be in the order of 10^4). The importance of the external diffusion resistance has been evaluated by making use of Mear's criterion

\[ \frac{(-r_{CH_4})F_0}{c_{CH_4}k_c} \]

(9)

\[ \frac{(-r_{CH_4})/r_0}{D_i c_{CH_4}} \]  

(10)

The parameters used to evaluate both inter- and intra-particle diffusion resistances have been summarized in Table 2. The mass transfer coefficient \( k_c \) has been estimated using the Thoenes–Kramers correlation [34]; the highest experimental methane reaction rate observed – detected at 850 °C, test 2 – has been taken as value for \( r_{CH_4} \), and used to calculate the dimensionless numbers at conditions where mass transfer limitations are most critical. The diffusion coefficient has been estimated considering binary diffusion of \( CH_4 \) in \( N_2 \) at 800 °C. The gas viscosity and density are estimated considering pure \( N_2 \) at 800 °C.

The left hand side of Mear’s equation has been found to be orders of magnitude lower than 0.15 (5 × 10^-5); as a consequence, external mass transfer limitations can safely be ignored. However, the Weisz–Prater criterion is not fulfilled, the left hand side of Eq. (9) being equal to 0.25. Therefore, diffusion limitation and concentration gradients inside the catalyst pellet do play an important role in the final observed reaction rate, and this effect has to be taken into account when deriving the intrinsic reaction kinetics. As a consequence, the FFR model has been coupled with a single particle model to describe the concentration profile inside the catalyst pellets, taking into account simultaneous reaction and diffusion. This is necessary, because the considered mechanism consists of several reactions with non-first order kinetics, and no accurate analytical efficiency model is available for this kind of problems.

The equations describing the concentration profiles inside the catalyst pellet are the following:

\[ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dc_i}{dr} \right) + \sum_{j=1}^{n_r} \nu_{ij} R_j = 0 \quad i = 1, 2 \ldots n_c \]

(10)

Table 2 Parameters governing Mear’s and Weisz-Prater criteria (see Notation section for symbols).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_0 )</td>
<td>2</td>
<td>mol kg^-1 s^-1</td>
</tr>
<tr>
<td>( F_0 )</td>
<td>6.25 × 10^-5</td>
<td>m</td>
</tr>
<tr>
<td>( \mu_c )</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>( \rho_c )</td>
<td>5.81</td>
<td>m s^-1</td>
</tr>
<tr>
<td>( \rho_0 )</td>
<td>1640</td>
<td>kg m^-3</td>
</tr>
<tr>
<td>( \rho_0 )</td>
<td>12.7</td>
<td>kg m^-3</td>
</tr>
<tr>
<td>( c_{CH_4}^0 )</td>
<td>5.4 × 10^-3</td>
<td>kmol m^-3</td>
</tr>
<tr>
<td>( U )</td>
<td>10.41</td>
<td>m s^-1</td>
</tr>
<tr>
<td>( Re )</td>
<td>9.5</td>
<td>-</td>
</tr>
<tr>
<td>( Sc )</td>
<td>6.8 × 10^-1</td>
<td>-</td>
</tr>
<tr>
<td>( Sh )</td>
<td>3.63</td>
<td>-</td>
</tr>
<tr>
<td>( D_{CH_4,N_2} )</td>
<td>2 × 10^-4</td>
<td>m^2 s^-1</td>
</tr>
<tr>
<td>( D_{eff} )</td>
<td>9.3 × 10^-6</td>
<td>m^2 s^-1</td>
</tr>
</tbody>
</table>
\[
dc_i = 0, \quad r = 0
\]
\[
c_i = c_i^0, \quad r = r_0
\]
(11)
(12)
where a Fickian description of the diffusion processes was used because of the large excess of \( \text{N}_2 \) used in the kinetic experiments. Note that this system of equations must be solved for all axial positions in the reactor. The second boundary condition (Eq. (12)) provides the coupling between the reactor mass balance equations and the particle sub-model. The production rates \( \{r_i\} \) in Eq. (6) are related to the diffusion fluxes of the single species at the pellet surface, as follows
\[
r_i = \left(-D_{i\text{N}_2} \left. \frac{dc_i}{dr} \right|_{r=r_0} \right) \frac{4\pi r^3 N_p}{6 V_f}
\]
where \( N_p/V_f \) is the number of catalyst particles in the total reactor volume and can be calculated as follows
\[
N_p/V_f = \frac{3\rho_b}{4\rho_c \pi r_0^3}
\]
where \( \rho_b \) is the bulk density of the catalyst (mass of catalyst per volume of bed), and \( \rho_c \) is the particle density of the catalyst (mass of catalyst per volume of catalyst pellet).

The kinetic equations considered for \( \text{CH}_4 \) oxidation, \( \text{CO} \) oxidation, \( \text{H}_2 \) oxidation and WGS reactions have been, respectively:
\[
R_1 = k_1 c_{\text{CH}_4} c_{\text{O}_2}^{1/2}
\]
\[
R_2 = k_2 c_{\text{CO}} c_{\text{O}_2}^{1/2}
\]
\[
R_3 = k_3 c_{\text{CO}_2} c_{\text{H}_2}^{1/2}
\]
\[
R_4 = k_4 \left( c_{\text{CO}_2} c_{\text{H}_2} - \frac{1}{K} c_{\text{CO}} c_{\text{H}_2} \right)
\]
(15)
(16)
(17)
(18)
where (1) the reaction orders have been chosen to match the reactions stoichiometry with respect to each reactant, (2) oxidation reactions \( R_1, R_2 \) and \( R_3 \) are considered as irreversible, (3) equilibrium is taken into account for water–gas shift reaction. The temperature dependency of all kinetic constants are described by the Arrhenius equation
\[
k_i = A_i e^{-\frac{E_i}{RT}} \quad (i = 1 \ldots 4)
\]
(19)
The equilibrium constant \( K \) for WGS was calculated from thermodynamics, with the following dependency on absolute temperature:
\[
\log_{10}(K) = -1.247 + \frac{8.269 \times 10^2}{T} - \frac{7.389 \times 10^5}{T^2}
- \frac{1.902 \times 10^8}{T^3} + \frac{1.850 \times 10^{10}}{T^4}
\]
(20)
The reaction kinetics is therefore described by 8 kinetic parameters in total. The optimal values for these parameters have been computed by means of a least square fitting of the experimental data.

5. Discussion

Results of the fitting procedure have been reported in Table 3, while Fig. 6 provides a parity plot of the calculated and measured outlet species molar fractions, showing a quite reasonable agreement between the experimental data and model results. Most of the points (\(-70\%\)) are within \( \pm 10\% \) error range, and almost all of them (\(-95\%\)) are within \( \pm 20\% \) range. In the zoomed parity plot (bottom of Fig. 6) different sets of horizontally aligned points are visible. These sets represent different series of experimental tests repeated at the same operating conditions: the model predicts the same results for

![Fig. 6. Molar outlet fractions parity plot: comparison between experimental observations and modeling outputs (on top), and enlargement of the small fractions area (on bottom).](image)

![Fig. 7. Calculated axial reaction rate profiles (reaction at 760 °C, inlet composition 13.1% CH₄, 4.5% O₂, 82.4% N₂).](image)
all the points of each series, whereas the variability in the x-axis reflects the experimental errors. In this way, Fig. 6 can give a better idea on the accuracy of the model. The activation energies and pre-exponential factors for the four reactions have been listed in Table 3.

**Table 3**

Calculated kinetic parameters $A$ (pre-exponential factor) and $E_a$ (activation energy) for the 4-reactions mechanism considered.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A$ (mol kg$_{cat}$ s$^{-1}$)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$ partial oxidation</td>
<td>$1.21 \times 10^7$</td>
<td>84.8</td>
</tr>
<tr>
<td>H$_2$ oxidation</td>
<td>$2.61 \times 10^5$</td>
<td>49.4</td>
</tr>
<tr>
<td>CO oxidation</td>
<td>$3.04 \times 10^4$</td>
<td>17.1</td>
</tr>
<tr>
<td>Water gas shift reaction</td>
<td>$1.71 \times 10^3$</td>
<td>102.2</td>
</tr>
</tbody>
</table>

From these values, the evolution of reaction rates as a function of the axial coordinate has been computed and an example is given in Fig. 7 (for test T3, first set of data of the base-case shown in Fig. S3). It is evident that CH$_4$ and H$_2$ oxidation reactions have a comparable reaction rates along the reactor length, but different trends are observed. Oxidation of CO is also important whereas the WGS reaction is the slowest reaction. CH$_4$ partial oxidation is dominant in the first part of the reactor, where the concentration of oxygen is maximum. Then its rate decreases along the axial coordinate, because of a decrease in both O$_2$ and CH$_4$ partial pressures; the rate of CO oxidation is more or less constant, whereas an increase in the H$_2$ oxidation reaction rate is observed along the axial coordinate due to the increase in the H$_2$ partial pressure. According to stoichiometry, two moles of hydrogen and only one mol of CO are produced by methane partial oxidation. Besides, WGS reaction rate
is positive which means that a little amount of the produced CO is converted to hydrogen. For these two reasons, the reaction rate of hydrogen oxidation is higher and increases more than the rate of CO oxidation.

Species molar fractions profiles simulated inside the catalyst particles are reported in Fig. S4 (supplementary information) for three different axial positions in the reactor (z=0, z=L/2, z=L respectively). It can be noted that there are indeed significant radial concentration gradients inside the particle, as anticipated because of the low value for the Weisz-Prater number. This is further evidence that intra-particle diffusion cannot be neglected in this process, even when relatively small catalyst particles are used as a result of the very high reaction rates. The concentration profile of H2 is less pronounced compared to the other species, because its diffusion coefficient is much larger than the others (about a factor 3).

Supplementary Fig. S4 related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2014.08.040.

Finally, the good agreement of experimental and computed outlet compositions is clear from Fig. 8, where several different feed compositions of CH4, O2, CO, CO2 and H2 are shown as example.

6. Conclusions

A LaCr0.85Ru0.15O3 perovskite-type catalyst was prepared which has shown high stability and selectivity to syngas production during catalytic tests performed at low GHSV. Physicochemical characterization of the LaCr0.85Ru0.15O3 perovskite precursor by XPS, TPR and XRD revealed that Ru is only partially incorporated into the LaCrO3 lattice and an important fraction of the loaded Ru exists as RuO2 surface species in close interaction with the chromite lattice. The high stability and exposition of these RuO2 species appears to be responsible for the high activity and low carbon deposition observed for this catalyst for the partial oxidation of methane.

Kinetic tests at high GHSV have been carried out and it has been found that reactors conversion and product selectivities can be described by a multi-parameter least square fitting, taking into account a four reactions mechanism involving CH4 partial oxidation, H2 and CO oxidation and water–gas shift. After separating the effect of intra particle diffusion resistance by means of a single particle sub-model, the activation energies and pre-exponential factors for these reactions have been calculated. The developed catalyst shows good promise to be used as catalyst in syngas generation processes such as reverse flow packed bed membrane reactors. The developed kinetic model can be used to describe and evaluate these processes, and appears to be reliable when the reaction is carried out in oxidizing atmosphere. Additional refinement in the model could be obtained considering data with low or zero oxygen concentration.

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