

**Syngas production by catalytic partial oxidation of methane over
(La_{0.7}A_{0.3})BO₃ (A=Ba, Ca, Mg, Sr, and B = Cr or Fe) perovskite oxides
for portable fuel cell applications**

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Abstract

Hydrogen is a clean energy carrier for future. More efficient, economic and small-scale syngas production has therefore important implications not only on the future sustainable hydrogen-based economy but also on the distributed energy generation technologies such as fuel cells. In this paper, a new concept for syngas production is presented with the use of redox stable lanthanum chromite and lanthanum ferrite perovskites with A-site doping of Ba, Ca, Mg and Sr as the pure atomic oxygen source for the catalytic partial oxidation of methane. In this process, catalytic partial oxidation reaction of methane occurs with the lattice oxygen of perovskites, forming H₂ and CO syngas. The oxygen vacancies due to the release of lattice oxygen ions are regenerated by passing air over the reduced nonstoichiometric perovskites. Studies by XRD, temperature-programmed reduction (TPR) and activity measurements showed the enhanced effects of alkaline element A-site dopants on reaction activity of both LaCrO₃ and LaFeO₃ oxides. In both series, Sr and Ca doping promotes significantly the activity towards the syngas production most likely due to the significantly increased mobility of the oxygen ions in perovskite oxide structures. The active oxygen species and performance of the LaACrO₃ and LaAFeO₃ perovskite oxides with respect to the catalytic partial oxidation of methane are discussed.

Keywords: Syngas; catalytic partial oxidation; Lanthanum chromite and ferrite perovskite; lattice oxygen; fuel cells.

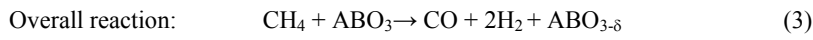
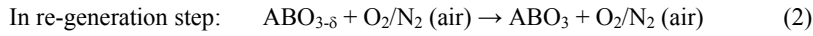
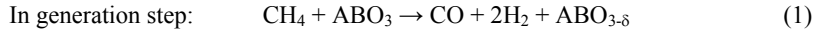
1. Introduction

Low cost production of hydrogen as a clean fuel is receiving increasing attention under the background of the resources depletion and the high price of petroleum oil [1]. A transition from fossil fuels to hydrogen and fuel cell technology in the next 50 years could diversify energy source, increase national security, and reduce environmental pollution and greenhouse gas emission. Under such situation, H₂ will then be produced not only in large scale in industrial areas, but also in fueling stations and customers' on-site applications in distributed scale[1, 2]. ~~Current commercial production of H₂ from natural gas involves primarily either steam methane reforming (SMR) or catalytic partial oxidation (CPO) [3, 4]. Catalytically converting methane to syngas is a significant route for methane utilization, since syngas could be used to produce hydrogen or generate electricity in fuel cells [5, 6].~~ There are three ways of converting methane to syngas, including the steam reforming of methane (SRM) [3, 74], the carbon dioxide reforming of methane (CRM) [85] and the catalytic partial oxidation of methane (CPO) [46]. ~~Current commercial H₂ production is based on SMR technology, an energy intensive and high CO₂ emission process. Particularly,~~ CPO has become the focus of researches ~~in recent years~~ due to its obvious advantages, such as high energy efficiency, suitable CO/H₂ ratio for methanol synthesis and Fischer–Tropsch processes [7-9]. However, pure O₂ via conventional, cryogenic separation of air is a major expensive capital investment for CPO-based syngas and hydrogen production, and it becomes increasingly expensive as unit size is scaled down. In general, these technologies, though highly optimized over years of development, remain probably too expensive and thus are not applicable for small-scale production of syngas for portable fuel cells.

Perovskite-type oxides with formula ABO_3 have received much attention over the past decades due to their high oxygen mobility and extensive applications in oxygen separation membranes [10-12], fuel cells [13-16], sensors [17], catalysts [18, 19], etc. In ABO_3 perovskite structure, A-site cation can be rare earth, alkaline earth, alkali and other large ions such as La^{3+} that will fit into the dodecahedral site of the framework, and B-site cation can be 3d, 4d or 5d transition metal ions which occupy the octahedral sites. These oxides can tolerate significant partial substitution and non-stoichiometry, while still maintaining the perovskite structure [20]. One of the unique properties of perovskites as catalysts is that perovskite-type oxides enable the generation of catalysts with active metals finely segregated onto a matrix or oxide surface produced *in situ* from an oxide precursor after reduction [21-24]. The highly dispersed metal particles diminishes deactivation of the catalysts and perovskite-type oxides have been extensively applied as catalysts for the partial oxidation of methane with CO_2 and O_2 [21, 22, 25-28].

It is also well known that lattice oxygen, O^{2-} , due to the oxygen-deficient nonstoichiometry in perovskites and oxygen conducting oxides plays an important role in the catalysis process such as dehydrogenation reactions and partial oxidation of methane [21, 29-32]. Watanabe et al [29] shows that reaction rate of dehydrogenation of ethylbenzene increases remarkably with the increase in the release rate of lattice oxygen of lanthanum barium manganite perovskite. In the case of partial oxidation of methane in the absence of gaseous oxygen, methane could react with mobile lattice oxygen via partial oxidation route, forming H_2 and CO . The oxygen vacancies, V_O generated during the catalytic oxidation reaction can be refilled by regenerating the oxygen-deficient perovskite oxides in oxygen or air, returning to normal stoichiometry composition. The generation

and re-generation steps continue, forming a cyclic operation to directly convert methane to syngas as shown below.



The syngas production and regeneration steps with redox stable ABO_3 perovskites as atomic oxygen source are schematically shown in Figure 1.

The proposed process as described here is simple and also low cost because the process does not require pure O_2 as oxidants and is reversible due to the high structural stability of perovskite oxides. Since the oxidation reaction occurs between CH_4 and lattice oxygen, O^{2-} there is no risk of explosion which may be caused by mixtures of CH_4 and gaseous pure O_2 . The selectivity of CO and H_2 would be expected to be higher than conventional CPO process since further oxidation of CO and H_2 (e.g., to CO_2 and H_2O) is limited due to the fact that there is no presence of gaseous oxygen.

To demonstrate the feasibility of the process, we selected lanthanum chromite and lanthanum ferrite perovskite oxides, $(\text{La}_{1-x}\text{A}_x)\text{CrO}_3$ and $(\text{La}_{1-x}\text{A}_x)\text{FeO}_3$ where A = Ba, Ca, Mg and Sr as oxygen source for the partial oxidation of methane for the syngas production. LaCrO_3 and LaFeO_3 are orthorhombic derivatives of the perovskite structure and exhibit high structural stability, oxygen ion conductivity and high catalytic activity for the application of interconnect and cathodes of solid oxide fuel cells [33-37]. It has been well

known that the catalytic activity and ionic conductivity of perovskite oxides can also be improved by partial substitution on A- and/ or B-sites [16, 38, 39].

2. Experimental

2.1 Synthesis of perovskite-typed oxides

Lanthanum oxide and the alkaline earth metal oxide, all of which were analytical reagent grade with purity > 99%, were used as initial materials for preparation of the $(\text{La}_{1-x}\text{A}_x)\text{BO}_3$ powders (A= Ba, Ca, Mg and Sr and B=Cr or Fe). The A-site substitution was 30 mol% for Mg, Ca and Ba and 25 mol % for Sr. The perovskite oxides were synthesized by solid-state reaction process, and the oxides with stoichiometric ratios were mixed by grinding and ball-milling in isopropanol for 5 hours, followed by calcination at 1200 °C for 5 h in air.

2.2 Material characterizations

Phase identification and crystal structures were investigated by x-ray powder diffraction (XRD, Philips 1710), with a Cu-K α radiation and a Ni filter, in the range of $2\theta = 15\text{--}85^\circ$. Specific surface area of the as-prepared perovskite oxide powders were determined by Brunauer, Emmett and Teller (BET) single point method over a QUANTACHROME Autosorb-6 instrument. Prior to analysis, the samples were degassed under vacuum, overnight. About 0.1 – 0.2 g of sample was used for each measurement. The changes in the oxygen deficiency of oxide samples were measured by temperature-programmed H₂ reduction (TPR), performed on Thermo TPD/RO 1100 Catalyst Analyzer System. A perovskite oxide sample of 50 mg was placed in a quartz micro-reactor and a

5% H₂/95% argon gas mixture with a flow rate of 50 ml/min was used as the reducing gas. The temperature was raised at a constant rate of 10 °C/min from 50 to 900 °C and maintained for 10 minutes before the test. Prior to the TPR testing the powder samples were pretreated at 300 °C for 30 min in air.

2.3 Measurement

Partial oxidation of methane over perovskites was studied by two experimental techniques, i.e., temperature-programmed surface reaction (TPSR) and steady state reaction (SSR) at 850 °C. The experimental setup is shown in Fig.2. For TPSR, 100 mg of the oxide sample was packed in a quartz tube micro-reactor ($\varnothing = 4$ mm), between layers of quartz wool. The sample was heated in the stream of 5 vol% CH₄ in Ar gas at a constant rate of 10 °C/min from room temperature to 950 °C. The effluent gas was analyzed on-line by mass spectroscopy (MS, Hiden HPR – 20 QIC). The reacted sample powders were then regenerated at 950 °C in 5% O₂/Ar at a flow rate of 50 ml/min with no change in the set up conditions.

Steady state reaction (SSR) was carried out in a continuous-flow fixed bed quartz micro-reactor (inner diameter = 10.3 mm, outer diameter = 12.0 mm) at atmospheric pressure packed with 250 mg samples that were sieved to a grain size of 180/300 μ m. The use of large quartz tube in this case is due to the increased catalyst loading. The sample temperature was raised at a constant rate of 10 °C/min from 50 to 850 °C in the flow of Ar and hold at 850 °C. A gas mixture of 5% methane in argon (carrier gas) with a total flow rate of 100 ml/min was passed through the sample in the quartz tube. The reaction products were detected by an online gas chromatography on a Shimadzu GC-2010

equipped with both a thermal conductivity detector (for H₂, CO, CH₄, CO₂ and N₂) and a flame ionizing detector (for C_xH_y and other products). Ar was used as the internal standard.

The conversion of CH₄, X_{CH_4} is defined as follows:

$$X_{CH_4} = \frac{mol_{CH_4 in} - mol_{CH_4 out}}{mol_{CH_4 in}} \times 100\% \quad (4)$$

3. Results and discussions

3.1 BET and XRD

Table 1 lists the composition and BET surface area for the as-prepared (La_{1-x}A_x)CrO₃ and (La_{1-x}A_x)FeO₃ perovskite samples. Due to the high calcination temperatures used in the sample preparation, the surface areas of the samples are generally low (≤ 5 m²/g). Among the oxides used, the lanthanum ferrite series have a higher surface area than that of chromite series.

Figure 3 displays the X-ray diffraction patterns of LaCrO₃ and LaFeO₃ in the forms of as-prepared after the catalytic oxidation (i.e., generation reaction (1)) and the regeneration reaction (2)). The as-prepared LaCrO₃ and LaFeO₃ show typical well-crystallized perovskite structures, indicating the successful synthesis of the LaCrO₃ and LaFeO₃ perovskite structure by the solid-state reaction method. After partial oxidation reaction in 5% CH₄ (Ar balanced) at 900 °C, traces of La₂O₃, La(CrO₃) and La(CrO₄) were observed in addition to LaCrO₃ perovskite main phase (Fig.3a), indicating minor or partial decomposition of LaCrO₃. However, after regeneration in 5%O₂/Ar at 950 °C, the XRD

peaks associated with La_2O_3 , $\text{La}(\text{CrO}_3)$ and $\text{La}(\text{CrO}_4)$ disappear completely and only the peaks for perovskite oxides remain, showing that the perovskite structure can be completely recovered after the regeneration in oxygen. This indicates that structural change during the catalytic oxidation of methane is reversible. In the case of LaFeO_3 there is no change in the perovskite-type structure after the catalytic oxidation in 5% CH_4 /95% Ar at 950°C (Fig.3b). This indicates that LaFeO_3 is quite stable for the catalytic oxidation in methane.

Figure 4 is the XRD patterns of the as-prepared doped LaCrO_3 and LaFeO_3 oxide series. Secondary phase of La_2O_3 was found in Ba and Mg doped LaCrO_3 (Fig.4a), probably due to the large size of the Ba and Mg dopants. In the case of Ca and Sr-doped LaCrO_3 , no secondary phases were found although a small shift to larger diffraction angle is observable for $\text{La}_{0.75}\text{Sr}_{0.25}\text{CrO}_3$ (Fig.4a), indicating the lattice distortion due to Sr substitution. Sr^{2+} ion is slightly larger than La^{3+} ion in size (0.144 vs. 0.136 nm). For the doped LaFeO_3 oxide series, Fe_2O_3 phase is observed in all doped samples, while Fe_2O_3 phase appears to be higher in the Sr and Ba doped samples (Fig.4b). Similar to Ba-doped LaCrO_3 , secondary phases were also observed in Ba-doped LaFeO_3 . Nonetheless, the peaks associated with perovskite oxides were dominant in all the XRD patterns, indicating the formation of main perovskite phases.

3.2. TPR

Temperature-programmed reduction (TPR) was carried out to study the oxygen mobility and the amount of oxygen which can be released from the oxides via the reaction with hydrogen. Figure 5 shows the TPR profiles of the amount of consumed hydrogen versus reaction temperature for the doped LaCrO_3 and LaFeO_3 oxide series. The amount of H_2 consumed per mole of the oxide sample can be obtained from calibrated integrated

peak areas in the TPR profile. For the undoped LaCrO_3 , the TPR profile is flat with no distinguish peaks, indicating no or little hydrogen was consumed by LaCrO_3 (Fig.5a). This also indicates that undoped LaCrO_3 has very low reducibility probably due to its very low activity and low ionic conductivity [40–42]. With alkaline earth (AE) metals dopants, one or more reduction peaks were observed, indicating the significant increase in the hydrogen consumption. However, the characteristics of the profile depend strongly on the nature of the dopant. For Ba-doped LaCrO_3 , there are three small adsorption peaks at 390, 485 and 590 °C, respectively. This may be related to the presence of multi-phases in Ba-doped LaCrO_3 (see Fig.4a). In the case of Sr-doped LaCrO_3 , the hydrogen consumption is characterized by a large and overlapped peak at around 550 °C. Two large reduction peaks were detected for the Ca-doped LaCrO_3 . The fact that both the reduction peaks are different in shape and height with the latter appearing at a high temperature could indicate the presence of different amount of active lattice O^{2-} species presence in the bulk and surface of the perovskite oxide that participate in the reaction at different temperatures.

For the undoped LaFeO_3 , a single peak with maximum at 662 °C is present (Fig.5b), showing higher activity as compared to that of the LaCrO_3 . With AE doping, the intensity as well as the number of reduction peaks increase significantly. For example, with Ca doping, a reduction peak was also observed at ~660 °C, but the intensity is 5 times higher than that of undoped LaFeO_3 . In the case of Sr-doped LaFeO_3 , two distinctive and large reduction peaks were detected at 505 and 900 °C, respectively. The distinctive reduction peaks at different temperatures could signify that there exist various types of O^{2-} species at different mobility which participate in the reaction with H_2 . These peaks with maxima at the temperatures in the range of between 250 and 900 °C could indicate the increased mobility of lattice oxygen ions by A-site doping with the AE metals. Similar to the doped

LaCrO₃ series, A-site doping changes significantly the TPR profile of LaFeO₃ samples. Although the TPR curves of the LaCrO₃ series have different profile as compared to that of LaFeO₃ series, it can be seen that in general, Sr and Ca doping promotes significantly the reducibility of perovskites, most likely due to the significantly increased mobility of the lattice oxygen ions in perovskite oxide structures.

The total amount of hydrogen consumed per mole of catalysts during TPR was calculated and the results are given in Table 2. The ratios of moles of hydrogen consumption per mole of catalysts indicate the variations in the availability or mobility of the oxygen lattice ions within the oxides. A high consumption implies the high availability of lattice oxygen, O²⁻ for the catalytic partial oxidation of methane (reaction (1)). The amount of hydrogen required for the reduction of one mole of catalyst is much lower for the LaCrO₃ series as compared to the LaFeO₃ series. The results are justifiable as LaFeO₃ is more readily reducible than the LaCrO₃[20]. In comparison, the undoped LaCrO₃ and LaFeO₃ have the smallest moles of H₂ consumed by one mole of catalysts, 0.08 and 0.12, respectively which suggested that both oxides have the least amount of lattice oxygen reacted. AE doping on A-site of ABO₃ perovskite greatly enhanced the oxygen availability. As it can be seen from Table 2, the amount of H₂ consumed by AE-doped LaCrO₃ and LaFeO₃ is one order of magnitude larger than their undoped counterparts. Among all the samples, the highest values obtained under each series are by the (La_{0.7}Ca_{0.3})CrO₃ and (La_{0.75}Sr_{0.25})FeO₃, which indicate that both (La_{0.7}Ca_{0.3})CrO₃ and (La_{0.75}Sr_{0.25})FeO₃ possesses the highest amount of active oxygen species that could be utilized for the catalytic oxidation of methane.

3.3. Catalytic partial oxidation of CH₄

Figure 6 shows the mass spectroscopy plots of the hydrogen production as a function of temperature when the perovskite oxides were exposed to 5%CH₄ in Ar from room temperature to 950 °C. Since small amount of perovskite oxides were used, 5% CH₄ was more than enough to react with the lattice oxygen.

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For undoped LaCrO₃, hydrogen production starts at ~800 °C and AE doping shifts the hydrogen formation temperature to lower temperatures and increases the hydrogen intensity (Fig.6a). Most of the H₂ peaks appear at temperatures from 820 to 900 °C for the doped LaCrO₃ oxides series with (La_{0.75}Sr_{0.25})CrO₃ having the highest intensity. In the case of Mg and Sr doped LaCrO₃, hydrogen production started at 750 °C and reached the maximum at ~820 °C. Ca-doped LaCrO₃ oxide gave two hydrogen formation peaks at 840 and 900 °C, respectively. This observation is consistent with the TPR result in Fig. 5a and could be due to the fact that different oxygen species in the Ca-doped LaCrO₃ sample is evolved at different temperature. Undoped LaFeO₃ also starts the hydrogen formation at ~800 °C but the intensity of the hydrogen formation is weak (Fig.6b), similar to that of undoped LaCrO₃. This indicates that both undoped LaCrO₃ and LaFeO₃ are very stable oxides with low activity for hydrogen production since the available oxygen for reaction is very limited as shown in Table 2. With the addition of AE metal dopants, the minimum temperatures needed for the partial oxidation of methane to syngas are reduced. Similar to the doped LaCrO₃ series, Sr-doped LaFeO₃ has the highest H₂ intensity at 853 °C.- The increment in H₂ production and methane activation ability of perovskites are correlated to the oxygen mobility and availability as shown in Fig.5 and Table 2.

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By using gas chromatography for on-line outlet gas analysis, as defined by Eq.(4), the amount of CH₄ converted was calculated and the syngas concentration in the outlet gas stream was measured for both doped LaCrO₃ and LaFeO₃ oxide series at 850 °C in the 5%

CH₄-95%Ar gas stream with GHSV of 750 h⁻¹. The results are shown in Fig.7. As seen in Fig. 7a, the CH₄ conversion on the doped LaCrO₃ oxide series is relatively low (<12%) and decreases gradually with the reaction time. The undoped LaCrO₃ oxide yields the lowest value of ~5% while the highest CH₄ conversion is 12% produced by Sr doped LaCrO₃. Though the CH₄ conversion decays at the first 70 mins, the highest conversion at the end of the test at 130 min was observed on Sr-doped LaCrO₃, 8% methane conversion. The La_{0.7}Ca_{0.3}CrO₃ oxide displays steady CH₄ conversion of 10% in the first 80 min, after which it drops rather quickly to 4%. The continuous decrease in the methane conversion rate indicates that the activity of doped LaCrO₃ decreases with the contact time with methane, most likely due to the gradual reduction in the amount of lattice oxygen available for the catalytic oxidation reaction.

Doped LaFeO₃ oxides have a much higher CH₄ conversion rate as compared to that of doped LaCrO₃ oxides counterpart. Also, very different from the continuous delay in methane conversion in the case of doped LaCrO₃, the activity of doped LaFeO₃ exhibits a significant induction period before reaching the maximum conversion rate (Fig.7b). For undoped LaFeO₃, the maximum conversion rate was 10% after reaction in 5%CH₄/Ar for 90 min. Doping LaFeO₃ with AE elements significantly shortens the induction period for the catalytic oxidation reaction as well as enhances the activity. In the case of Sr doped LaFeO₃ the maximum conversion rate of 60% occurs at 65 min and the best activity and performance was observed for the Ca doped LaFeO₃, 70% conversion at ~30 min. For Mg doped LaFeO₃ it took ~120 mins to reach a maximum conversion rate of 65%.

The production rate of hydrogen and CO on doped LaCrO₃ and LaFeO₃ oxides basically follows that of methane conversion (see Fig.7c-f). As illustrated in Fig. 7c, the H₂ concentration for undoped LaCrO₃ and Ba-doped LaCrO₃ are basically constant at 0.5

and 0.8% correspondingly. Sr doped LaCrO_3 produces 2.4% of H_2 and decreased to a steady value of 1.0% after reacted for 80 min. The Ca dopant shows rather high yield of H_2 production, which decreases gradually from 2.25% to 1.5% in the first 60 min on stream, and then remains steadily at the 1.5% in the next 80 min. Mg dopant displays comparable trend, decreasing from 2.25% to 1.0%. Similar trend was also observed for the CO concentration on doped LaCrO_3 oxide series (Fig.7e).

Doped LaFeO_3 oxides show increasing patterns for the H_2 production with reaction time (Fig. 7d). For LaFeO_3 the H_2 production increases to 2% after reaction for 90 min after which remains at that value over the holding time of 140 min. The Sr doped oxide displays rather a steady increasing H_2 production in the first 60 min, reaches a maximum of 10% and maintains for another 10 min, followed by continuous decline to 1%. The Ba dopant follow similar trend with a gradual increase to 7%, and decreases to 1% in the next 80 min holding time. The $\text{La}_{0.7}\text{Ca}_{0.3}\text{CrO}_3$ increases from initial value of 3% to 9% in the 60 min stream on line time. The Mg dopant takes a longer time to be activated to give a raise from 0 to 11% in the 120th min. Similar trend was also observed for the CO production (Fig.7f).

Fig.8 is the molar ratio of H_2 to CO for both oxide series. The data were taken from Fig.7c to Fig.7f. The H_2 to CO molar ratio for the undoped LaCrO_3 and LaFeO_3 samples is approximate 2 which is the theoretical value derived from partial oxidation of methane, according to reaction (3). Doping generally enhances H_2/CO ratio. LaMgCrO_3 , LaSrCrO_3 , LaMgFeO_3 , LaBaFeO_3 and LaSrFeO_3 are seen to maintain the H_2/CO ratio steady at various levels between 2 and 6 within 80 min testing. The high H_2/CO ratios indicate the occurrence of CH_4 cracking. The most likely reason may be due to the fact that fine AE dopant could be segregated on the oxide surface *in situ* during the CPO of methane [21-24]

and induces the methane cracking. Another possible reason for the higher H₂ concentration could be due to part of Fe was reduced by H₂ during the reaction and catalyzed the methane cracking.

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Thus it can be concluded that the doping of alkaline earth metals improves both the CH₄ conversion and syngas production. The selectivity of H₂ was found to be 100% and that of CO was nearly 100% with no H₂O and CO₂ produced. The LaAFeO₃ oxides are active in the oxidative conversion of methane to syngas as the CH₄ conversion and syngas concentration remained steady during the experimental period of 140 min. Among the doped LaACrO₃ series, Ca²⁺ doped oxide yielded better activity and higher syngas concentration. Despite having a slightly low methane conversion of 10%, La_{0.7}Ca_{0.3}CrO₃ outperformed the rest giving a high steady concentration: 2.25% H₂ and 0.7% CO. Methane conversion of 12% with 2.25% H₂ and 1% CO concentration was also achieved by La_{0.75}Sr_{0.25}CrO₃. In the case of the doped LaFeO₃ series, CH₄ conversion is significantly high. Best results were obtained on Ca²⁺ and Sr²⁺ doped LaFeO₃ oxides. La_{0.7}Ca_{0.3}FeO₃ gave a 70% of CH₄ conversion with 10% H₂ and 2.5% CO within 50 mins, while La_{0.75}Sr_{0.25}FeO₃ achieved a 65% CH₄ conversion, 10% H₂, and 2.8 % CO within 50 mins. In conclusion, Ca and Sr are the best dopants for both LaCrO₃ and LaFeO₃ for the catalytic oxidation of methane. This is most likely correlated to the high oxygen availability of Ca and Sr doped LaCrO₃ and LaFeO₃ perovskites.

4. Conclusion

Polycrystalline AE metal doped LaCrO₃ and LaFeO₃ oxides have been prepared by conventional solid state reactions and the potential of these two series of perovskite oxides as atomic oxygen sources for the partial oxidation of methane to syngas was studied. A-

site doping with AE metals generally increases the mobility of lattice oxygen ions and thus decreases the temperatures for the hydrogen and CO production, as compared with the undoped LaCrO_3 and LaFeO_3 oxides. The minor structural change during the partial oxidation of methane in the case of LaCrO_3 can be regenerated by oxidation in O_2/Ar at 950 °C, while LaFeO_3 showed negligible structural changes during the catalytic oxidation reaction of methane. The results indicate stable activities of the perovskites during the repeated reaction cycles of generation-regeneration. LaAlFeO_3 series yield better performance than the LaACrO_3 series. The best results were obtained on $(\text{La}_{0.75}\text{Sr}_{0.25})\text{FeO}_3$ with 65% of CH_4 conversion, 10 % H_2 and 2.8% CO production at 850 °C with 100% H_2 selectivity. The high activity of $(\text{La}_{0.75}\text{Sr}_{0.25})\text{FeO}_3$ is most likely due to the highly mobile lattice oxide ions, indicated by the low reducing temperature (~ 400 °C) in H_2 and a high mole ratio of 1.37 (H_2 consumed per catalyst used). $(\text{La}_{0.75}\text{Sr}_{0.25})\text{FeO}_3$ shows a promising potential as atomic oxygen source for syngas production via the reaction of methane for portable fuel cells applications.

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Figure captions:

1. Syngas production and regeneration steps over ABO_3 perovskite oxides.
2. Schematic diagram of the experimental set-up.
3. XRD patterns of (a) as-prepared LaCrO_3 , LaCrO_3 after generation in 5% CH_4/Ar at 900°C, and LaCrO_3 after regeneration in 5% O_2/Ar at 950°C; and (b) as-prepared LaFeO_3 , LaFeO_3 after generation in 5% CH_4/Ar at 950°C, and LaFeO_3 after regeneration in 5% O_2/Ar at 950°C.
4. XRD patterns of the as-prepared (a) doped LaCrO_3 oxides and (b) doped LaFeO_3 oxide series.
5. TPR profiles of (a) doped LaCrO_3 and (b) doped LaFeO_3 oxides, showing the intensity, temperature and time on stream at which H_2 is consumed from the reaction between H_2 and perovskite oxides. The flow rate was 50 ~~ml~~ ml/min of 5% H_2/Ar , and the weight of each sample is 50 mg. The temperature was raised at a rate of 10 °C/min from room temperature to 900 °C.
6. MS profiles of oxidation of methane (5% CH_4/Ar) over (a) doped LaCrO_3 and (b) doped LaFeO_3 oxides, showing the intensity and temperature at which H_2 is produced and detected by mass spectrometer. The flow rate was 100 ml/min of 5% CH_4/Ar , and the weight of each sample is 100 mg. The temperature was raised at a rate of 10 °C/min from room temperature to 950 °C.
7. Plots of catalytic activity of partial oxidation of methane of 5% CH_4 , measured at 850°C, GHSV of 750 h^{-1} over doped LaCrO_3 and LaFeO_3 oxides respectively: (a, b) CH_4 conversion, (c, d) H_2 concentration, and (e, f) CO concentration.
8. Plots of molar ratio of H_2/CO produced over (a) doped LaCrO_3 and (b) doped LaFeO_3 oxides. The data were taken from Fig.7c-f.

Table 1. BET surface areas of as-prepared (La_{1-x}A_x)MO₃ perovskites-type oxides.

Surface area (m ² /g)		Surface area (m ² /g)	
LaCrO ₃	2.39	LaFeO ₃	2.99
(La _{0.7} Ba _{0.3})CrO ₃	2.57	(La _{0.7} Ba _{0.3})FeO ₃	3.72
(La _{0.7} Ca _{0.3})CrO ₃	3.21	(La _{0.7} Ca _{0.3})FeO ₃	4.76
(La _{0.7} Mg _{0.3})CrO ₃	2.76	(La _{0.7} Mg _{0.3})FeO ₃	5.02
(La _{0.75} Sr _{0.25})CrO ₃	2.78	(La _{0.75} Sr _{0.25})FeO ₃	4.97

Table 2. Number of mole of H₂ being consumed per mole of perovskite oxides used, tabulated from the TPR results for the (La_{1-x}A_x)MO₃ perovskites-type oxides.

	Moles of H ₂ Consumed per one mole of Catalyst
LaCrO ₃	0.08
(La _{0.7} Ba _{0.3})CrO ₃	0.27
(La _{0.7} Ca _{0.3})CrO ₃	0.60
(La _{0.7} Mg _{0.3})CrO ₃	0.20
(La _{0.75} Sr _{0.25})CrO ₃	0.38
LaFeO ₃	0.12
(La _{0.7} Ba _{0.3})FeO ₃	1.03
(La _{0.7} Ca _{0.3})FeO ₃	1.11
(La _{0.7} Mg _{0.3})FeO ₃	1.26
(La _{0.75} Sr _{0.25})FeO ₃	2.65

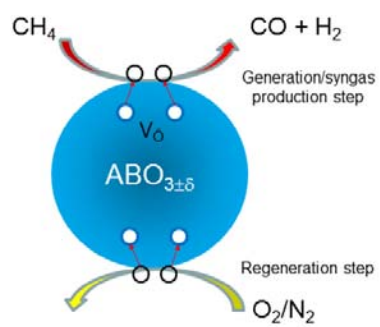


Figure 1.

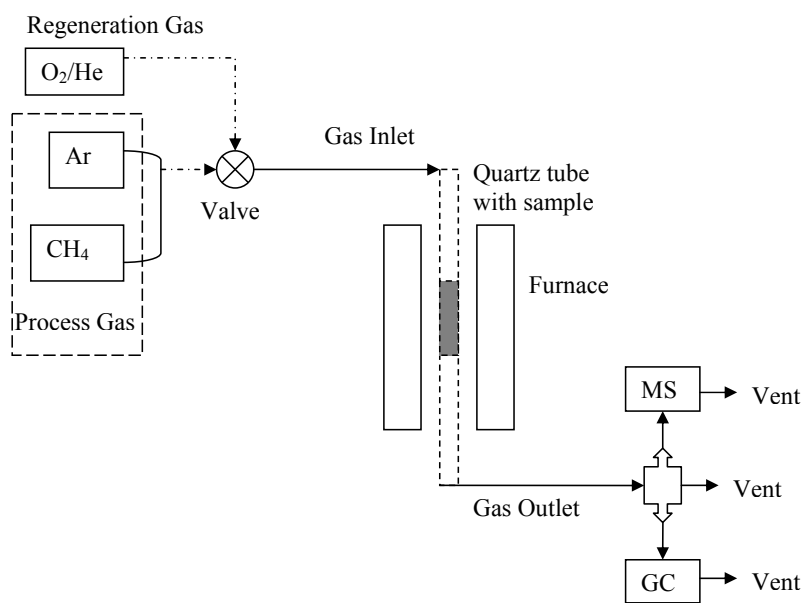


Figure 2.

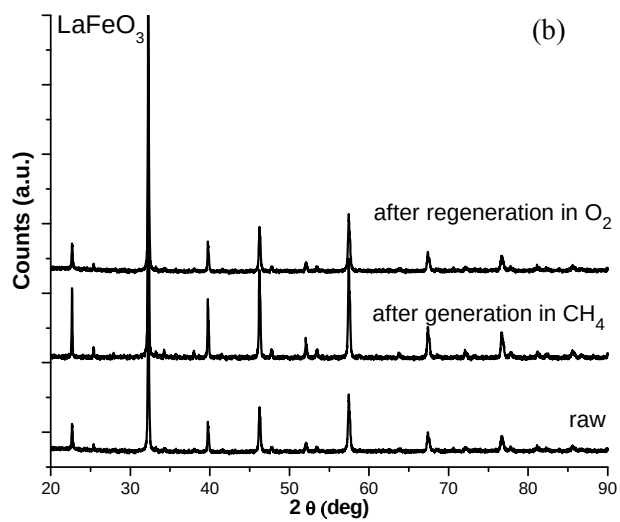
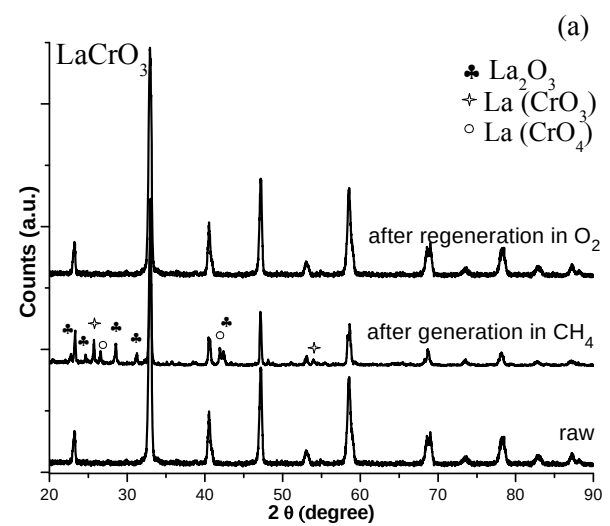


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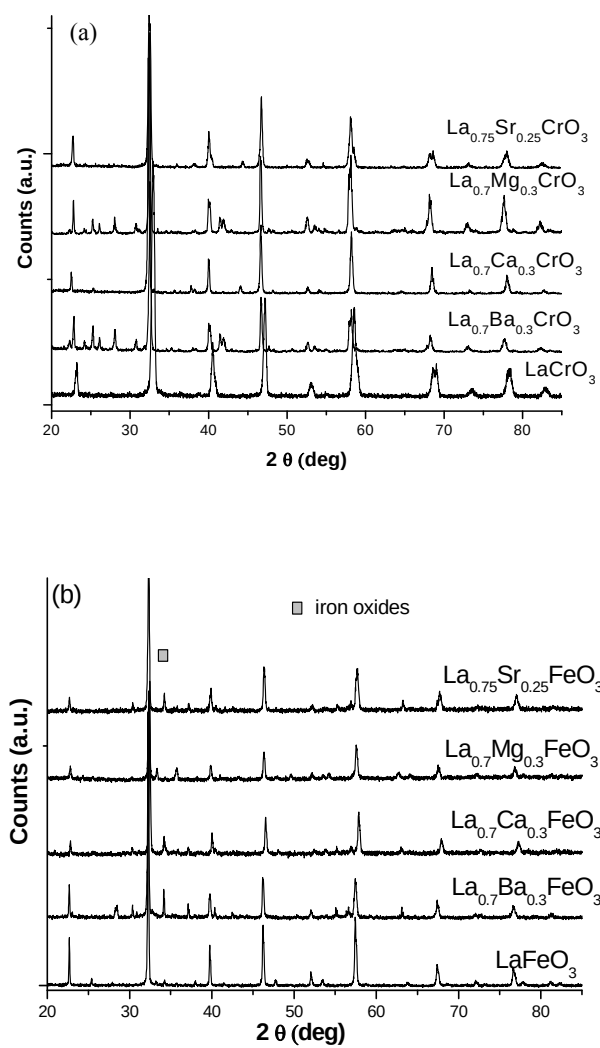


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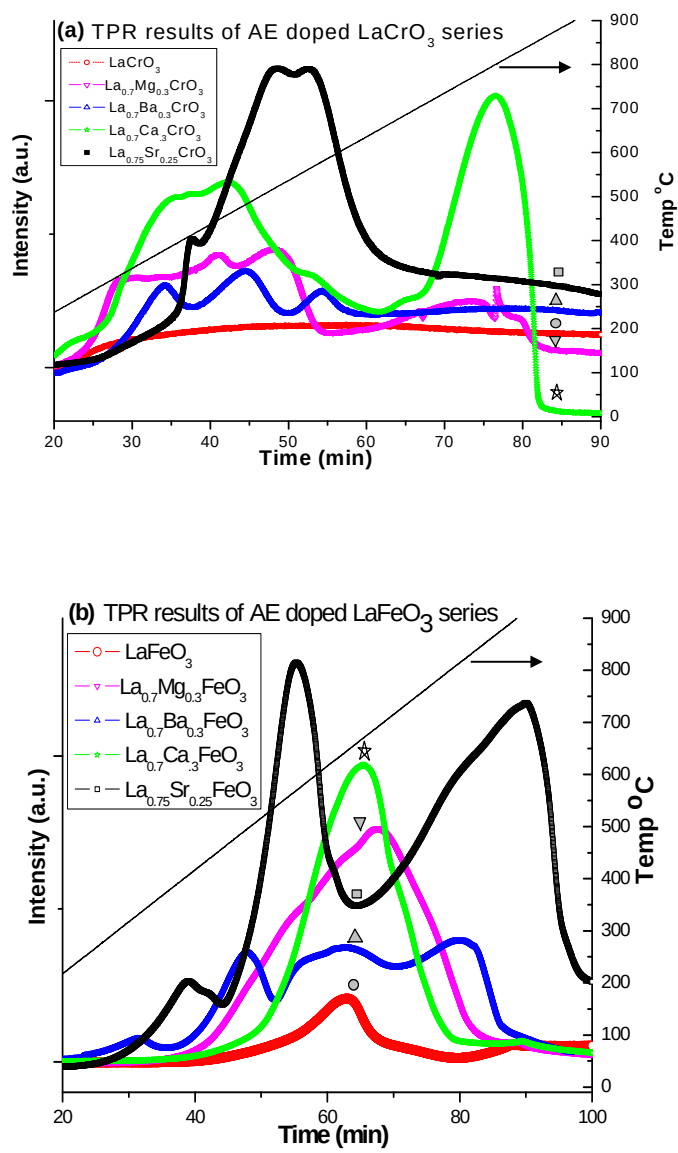


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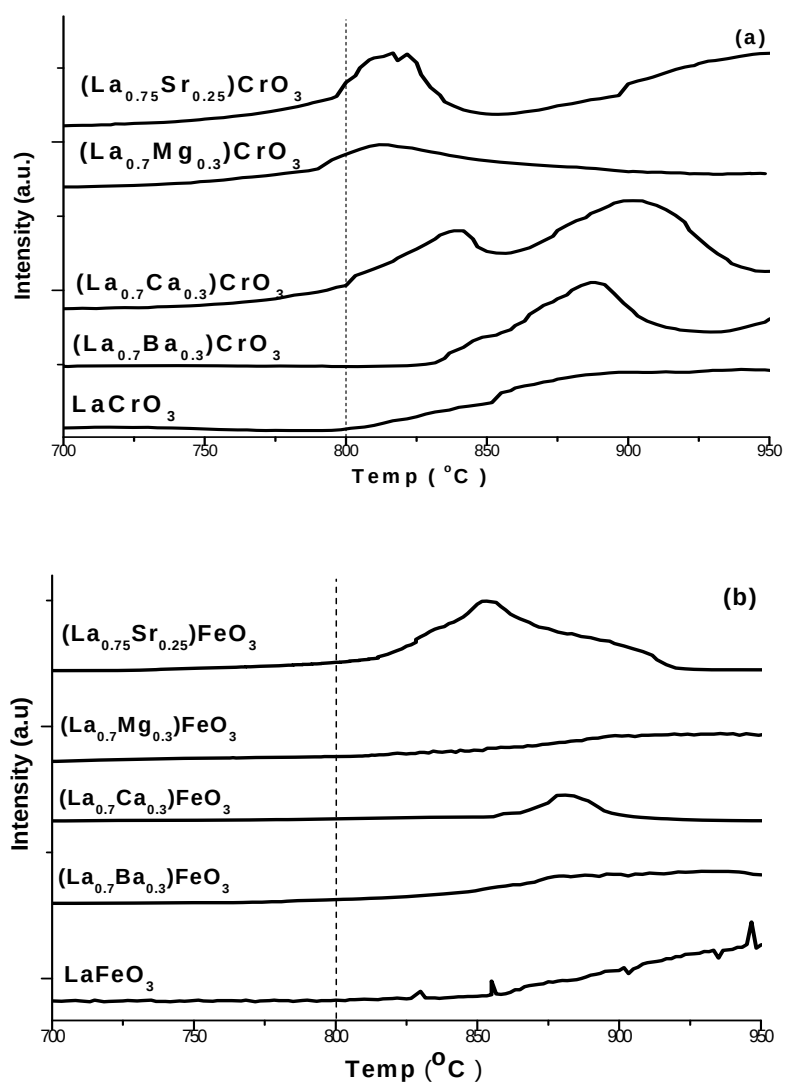
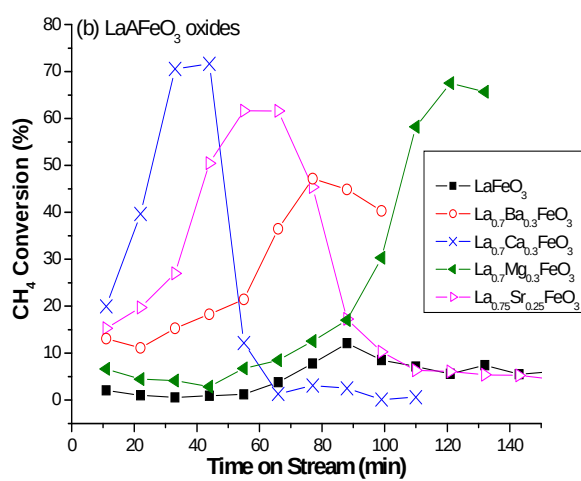
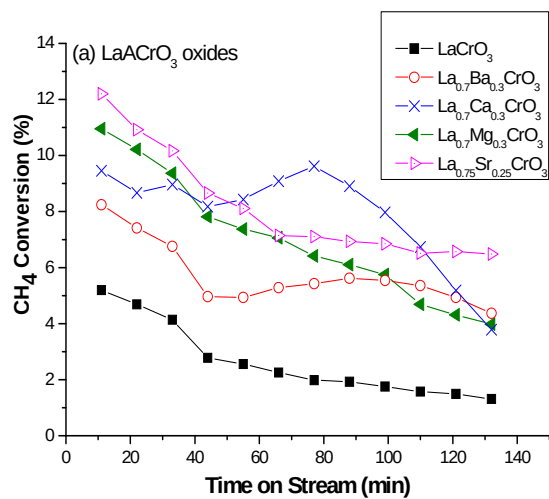
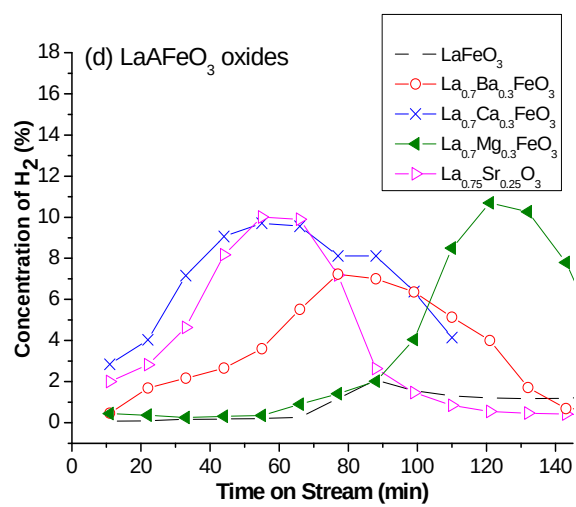
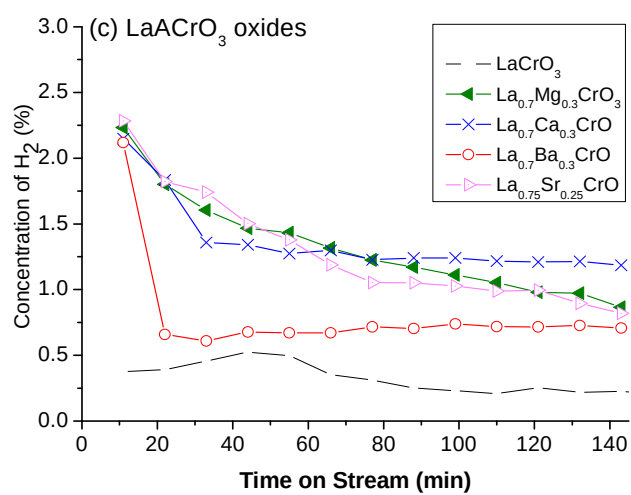


Figure 6.





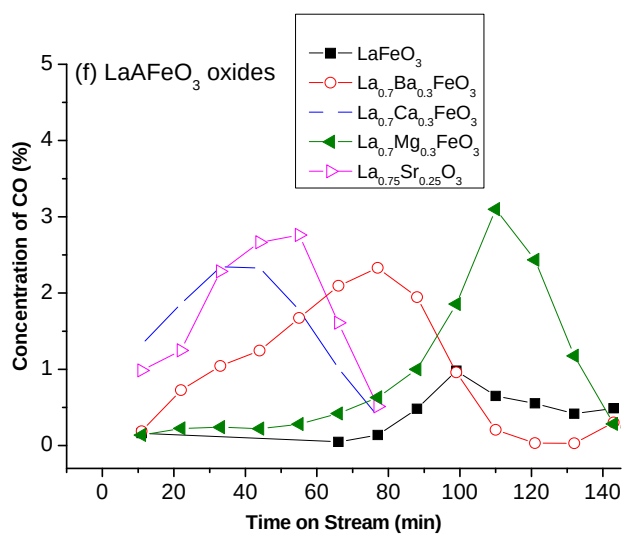
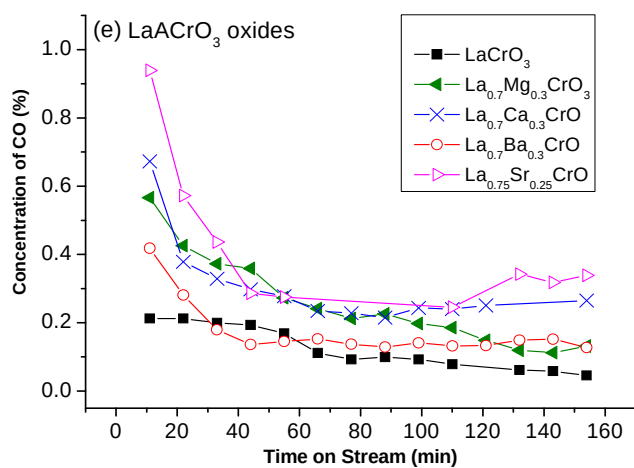


Figure 7.

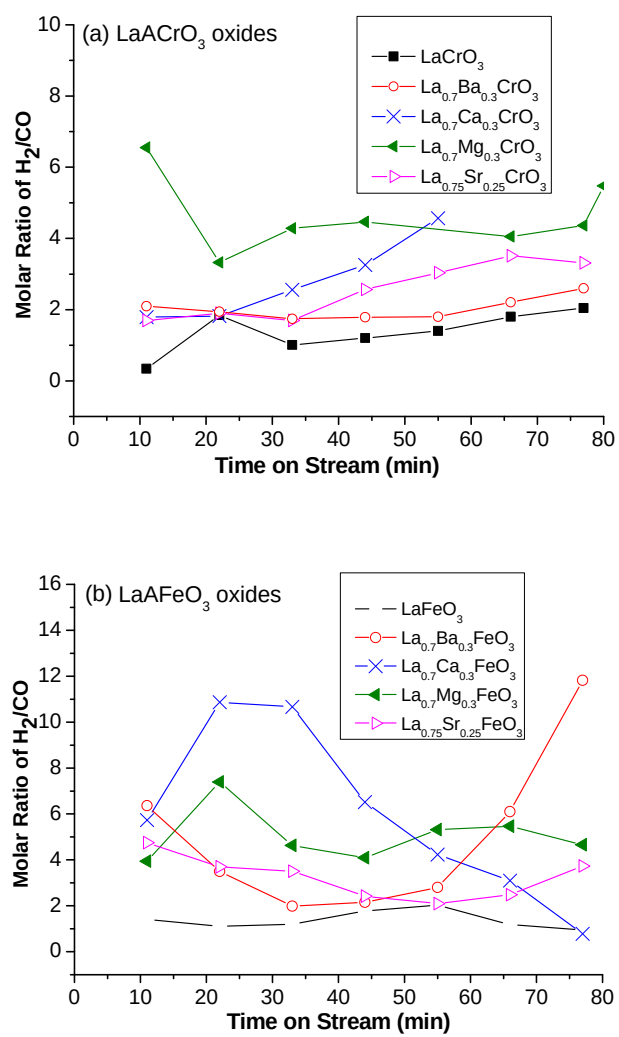


Figure 8.